Universidad de Valladolid

ESCUELA DE INGENIERÍAS INDUSTRIALES

DEPARTAMENTO DE INGENIERÍA QUÍMICA Y TECNOLOGÍA DEL MEDIO AMBIENTE

TESIS DOCTORAL:

EVALUACIÓN DE LA BIODEGRADABILIDAD ANAEROBIA DE RESIDUOS ORGÁNICOS PRE-TRATADOS TÉRMICAMENTE

Presentada por Liliana Catarina Gonçalves Ferreira para optar al grado de doctor por la Universidad de Valladolid

Dirigida por:

Dr. Sara Isabel Pérez Elvira

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ESCUELA DE INGENIERÍAS INDUSTRIALES

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Valladolid, a ______ de________________ de 2013

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Certifica que:

Liliana Catarina Gonçalves Ferreira ha realizado bajo su dirección el trabajo *"Evaluación de la biodegradabilidad anaerobia de residuos orgánicos pre-tratados térmicamente"*, en el Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Escuela de Ingenierías Industriales de la Universidad de Valladolid. Considerando que dicho trabajo reúne los requisitos para ser presentado como Tesis Doctoral expresan su conformidad con dicha presentación.

Valladolid, a ______ de_______________ de 2013

Fdo. Sara Isabel Pérez Elvira

Reunido el tribunal que ha juzgado la Tesis Doctoral titulada *"Evaluación de la biodegradabilidad anaerobia de residuos orgánicos pre-tratados térmicamente"* presentada por Liliana Catarina Gonçalves Ferreira y en cumplimiento con lo establecido por el Real Decreto 99/2011 de 28 de enero de 2011 acuerda conceder por_______________ la calificación de _________________________.

Valladolid, a ______ de_______________ de 2013

PRESIDENTE SECRETARIO

1er Vocal 2º Vocal 3er Vocal

AGRADECIMIENTOS

Ha sido un largo camino. No lo digo que fácil pero, tampoco así lo pensaba. Lo que importa es que fuera posible.
Y lo fue… cuatro años después me veo intentando agradecer a todos aquellos que han hecho parte de este camino. Lo intentaré, aún que sepa que siempre quedará alguien olvidado… lo siento!

En primero, agradezco al Profesor Fernando Fdz-Polanco por la oportunidad de hacer parte de este proyecto y con el poder desarrollar mi tesis. Gracias por todos los conocimientos que me has transmitido. Gracias por estar siempre presente como profesor pero también como consejero y amigo. Gracias por hacerme sentir en casa.

A ti Sara, te agradezco la confianza que has depositado en mí para seguir con este proyecto. Como tutora y amiga has estado siempre en los momentos más importantes. Gracias por todo lo que me has enseñado y apoyado.

A las demás profesoras que he tenido la suerte de conocer, María Fdz-Polanco y Mar Peña, gracias por vuestro cariño.

A la empresa Cambi®, le agradezco el financiamiento del proyecto que ha permitido desarrollar mi trabajo.

Cuatro años lejos de la familia me han permitido conocer otras culturas y crecer a todos los niveles. He crecido con los compañeros en el departamento, pero aquí también he tenido mi segunda familia. He ganado amigos que no los olvidaré, compañeros de los malos y buenos momentos.

Amigos Andrea Carvajal, Raúl Muñoz, Guillermo Quijano, João Gouveia… a vosotros os debo una infinita gratitud por todo el apoyo y cariño a lo largo de toda mi estancia. Gracias por vuestra compañía diaria, por tener siempre una palabra alegre.
A ti Raúl Muñoz… un agradecimiento especial… no olvidaré tu mano amiga en horas difíciles…

Araceli… amiga, compañera, hermana… no tendré palabras posibles para describir toda la verdadera amistad y gratitud. He ganado una segunda hermana… gracias por estar ayer, hoy y siempre presente. Por los momentos juntas, en que hemos reído, llorado, por lo que nunca olvidaré. Adonde yo esté tendrás siempre tu casa… te quiero mucho!

Compañeros Ana Nielfa, Raúl Cano, Iris Ramos, Lara Pérez, Jaime, Theo… por los momentos que hemos compartido, en los que hemos podido trabajar juntos pero también reír y disfrutar… serán siempre momentos en mis recuerdos. Gracias por vuestra compañía! Esther Posadas, gracias por tu amistad y por lo por el día en que me has enseñado el poema que pongo al final.
Rebeca, João Queiroz, Esther Alonso, Alexander, Oscar… gracias por la compañía y los ánimos diarios en el despecho que hemos compartido.
Sílvia, Sara Santamarta, gracias por vuestra ayuda en mi análisis de laboratorio y sin duda por vuestra amistad.

A mí familia…

Aos que tudo devo… um apoio incondicional, presente a cada dia. Nos momentos em que tudo parecia não ser suportável… sempre estivestes!

Mamã, papá… juntos conseguimos. Sim… porque sozinha era impossível percorrer semelhante caminho. E por final, ainda vos tocou uma parte da vida de emigrante… enfim só mesmo pais como vós! Obrigada!

A vós minha irmã e meu cunhado… a distância tornava-se pequena a cada dia que o telefone tocava. E no pior momento… aquele no outro lado… lá estáveis vós… obrigada!

A vós os quatro vos devo cada dia de felicidade, de força e cada pedra retirada do caminho.

Madrinha, obrigada por estares sempre presente. Obrigada pelo ânimo e por me fazeres acreditar que era possível.

Aos meus tios, Maria Elisa e Né, por todo o carinho e força.

A vós primos, Jorge e Néné, por me ajudares a entender este mundo da ciência.

Família… um eterno agradecimento.

Caminante, son tus huellas
el camino y nada más;
Caminante, no hay camino,
se hace camino al andar.
Al andar se hace el camino,
y al volver la vista atrás
se ve la senda que nunca
se ha de volver a pisar.
Caminante no hay camino
sino estelas en la mar.

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Resumen

Una primera revisión bibliográfica relativa al estado del arte en materia de residuos y energía en España puso de manifiesto que tanto en la legislación (Ley 22/2011) como en los planes de Energías Renovables en España (PER, 2005-2010) y el Plan Integrado de Residuos (PNIR, 2008-2015) se ha establecido como prioridad la valorización de los residuos orgánicos por la vía de la generación de biogás.

Marcando por tanto como objetivo global la OPTIMIZACIÓN DE LA DIGESTIÓN ANAEROBIA DE RESIDUOS ORGÁNICOS, la presente tesis comenzó con la realización de una investigación bibliográfica específica con los objetivos de definir los residuos de mayor interés y evaluar la problemática de su digestibilidad. Dada la limitación de la etapa de hidrólisis para residuos particulados, el rumbo de la tesis quedó fijado en la introducción de una etapa previa de pre-tratamiento, obteniéndose financiación de la empresa Cambi, líder mundial en tecnologías de tratamiento térmico de residuos.

De este modo, la temática y objetivo final se concretan en la OPTIMIZACION DE LA DIGESTIÓN ANAEROBIA DE DISTINTOS RESIDUOS ORGÁNICOS MEDIANTE LA INTRODUCCIÓN DE UN PRE-TRATAMIENTO DE HIDRÓLISIS TÉRMICA CON EXPLOSIÓN DE VAPOR. Y como materia prima se seleccionan residuos de distintas categorías: industriales (bagazo de cerveza y cáscara de naranja), agrícolas (paja de trigo), ganaderos (purín de cerdo) y urbanos (lodos de depuradora), y se plantea una sistemática de trabajo común: experimentación en planta piloto de hidrólisis térmica con explosión de vapor en distintas combinaciones de temperatura-tiempo en el rango 150-220ºC y 1-60 minutos (unificadas en un “factor de severidad”), y evaluación de la influencia en la biodegradabilidad mediante ensayos *batch* de potencial metanogénico, y estudio matemático cinético y estadístico de los resultados.

El inicio de la tesis no resultó esperanzador, dado que los resultados con los dos residuos industriales ensayados mostraron que la hidrólisis térmica no mejoró la biodegradabilidad de dichos residuos; por el contrario, tanto la productividad como la cinética empeoraron.
Hasta este momento, el único parámetro que se empleó en la discusión fue el factor de biodegradabilidad, que compara la producción de metano del residuo tratado respecto del no tratado.

La paja de trigo fue el tercer residuo ensayado, obteniéndose resultados positivos en productividad para pre-tratamientos de severidad moderada, mostrando que no siempre el pre-tratamiento resulta beneficioso. Las condiciones óptimas de operación resultaron 200ºC-5min y 220ºC-1min (factor de severidad de 3.5), para las cuales la producción de metano se incrementó en un 20-25% y la velocidad de degradación se duplicó.

En el caso del purín de cerdo, pre-tratado en el rango 120-180ºC, el tratamiento térmico siempre resultó beneficioso, llegándose a doblar tanto la productividad de metano como la velocidad de degradación para las condiciones óptimas de 170ºC y 15-30 min (factor de severidad de 3.5).

Finalmente, para el residuo de lodos de depuradora, dado que la optimización de las condiciones de hidrólisis térmica ya ha sido previamente estudiada en una serie de trabajos publicados por miembros del grupo de investigación dentro del que se desarrolla la presente tesis (Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Universidad de Valladolid), el estudio realizado en el marco de esta tesis ha consistido en la implementación del modelo Anaerobic Digestión Model Nº1 para el modelado del comportamiento de digestores alimentados con lodo pre-tratado térmicamente. Previamente calibrado mediante resultados obtenidos en ensayos BMP, el modelo resultante ha demostrado ser fiable y útil.

A partir de los resultados obtenidos se planteó una evaluación energética con el objetivo de tener una primera visión de la relación entre la energía térmica requerida para el funcionamiento del pre-tratamiento y la energía térmica generada a partir de biogás.

Para los tres residuos cuyo pre-tratamiento ha resultado de interés (paja de trigo, purines de cerdo y lodos de depuradora), el balance resultó positivo. Sin embargo, el interés real desde el punto de vista operacional radica en las opciones de co-tratamiento y co-digestión, dada la posibilidad de incrementar la carga de operación de los digestores alimentados con residuo pre-tratado, y los incrementos reales de producción global de biogás que pueden obtenerse de este modo (más allá de los incrementos de productividad obtenidos en los ensayos de BMP).

Existe, por tanto, un campo de trabajo abierto a partir de esta tesis, que se apoye en la operación de digestores en continuo alimentados con mezcla de residuos pre-tratados y frescos.

Capítulo 1

Antecedentes Generales

1.1 Introducción: ¿Residuos o recursos?

La generación de residuos es una consecuencia directa de cualquier tipo de actividad desarrollada por el hombre; hace años un gran porcentaje de los residuos eran reutilizados en muy diversos usos, pero hoy en día nos encontramos en una sociedad de consumo que genera gran cantidad y variedad de residuos procedentes de un amplio abanico de actividades. En los hogares, oficinas, mercados, industrias, hospitales, etc., se producen residuos que es preciso recoger, tratar y eliminar adecuadamente.

Los residuos constituyen uno de los problemas ambientales más graves de las sociedades modernas, en particular de las más avanzadas e industrializadas. Se trata de un problema en aumento, que no deja de agravarse debido al creciente volumen generado y la estrecha relación de paralelismo entre los niveles de renta y de calidad de vida y el volumen de residuos que generamos. Esta negativa circunstancia se agrava por la aún insuficiente concienciación ciudadana en esta materia, que dificulta con frecuencia la adopción de la mejor solución posible para determinados residuos.

De acuerdo con las estadísticas de la Naciones Unidas, la población mundial en 2050 superará los 9 mil millones. La combinación del efecto del crecimiento de la población y las tendencias de consumo conducen a un mayor consumo de recursos, esto es, mayor demanda de energía, agua y nutrientes, y a un aumento exponencial de los residuos. Este aumento de los residuos provoca directamente el incremento de la polución del planeta y la contaminación del medio ambiente. Por ello, **mejorar la eficiencia en la utilización de los recursos y en la gestión de los residuos no es solo una necesidad sino un desafío.**

Por otro lado, el tratamiento de los residuos exige un coste elevado. Se presenta entonces la necesidad de la búsqueda de la reducción de costes de su tratamiento, bien por la mejora de técnicas conocidas o por la aplicación de nuevas tecnologías que resulten no sólo eficientes sino económicamente viables.

Por todo lo expuesto, desde el punto de vista práctico (económico, medioambiental y social) resulta de gran interés el concepto de **residuo como recurso**, esto es, su valorización tanto agrícola (aplicación al suelo) como energética (como fuente de energía). Teniendo en cuenta que hoy en día los combustibles fósiles representan aproximadamente el 80% de la energía consumida por la humanidad, la obtención de bioenergía (proveniente de materiales biológicos) es una opción enormemente atractiva.

1.2. Revisión del estado del arte sobre residuos sólidos orgánicos en España

1.2.1. Los residuos sólidos y su clasificación

El carácter que define a un material como residual no es tanto el interés o no de su generación, sino el hecho de que se forma como subproducto sobrante de una operación o actividad, tanto en los procesos intermedios como por el uso o consumo final. Así, se entiende por residuo todo material o sustancia inútil, o no deseado, que es abandonado por quien lo genera, y que es susceptible de aprovechamiento o transformación en un nuevo bien, con valor económico o para disposición final.

Otra definición de residuo es la recogida en la Ley 22/2011 de residuos y suelos contaminados, donde residuo es “cualquier sustancia u objeto que su poseedor deseche o tenga la intención u obligación de desechar”.

La gran cantidad y variedad de residuos generados hace que se recurra a clasificarlos para facilitar su estudio y optar por el sistema de gestión más adecuado de los mismos.

La composición media de los residuos urbanos en España está formada por el 44% de materia orgánica, 21% papel-cartón, 10.6% de plástico, 7% vidrio, 4.1% metales, 1% maderas y 12.3% de otros (PNIR 2007-2015). Como se puede observar, 65% está formado por residuos biodegradables.

El modo de clasificar los residuos puede ser muy variado, ya que se pueden establecer clasificaciones atendiendo a distintos criterios, como son:

- Origen: Residuos industriales, agrícolas y ganaderos, sanitarios, urbanos y biorresiduo.
- Características físico-químicas: Residuos sólidos, líquidos, emisiones gaseosas, lodos/fangos, residuos pastosos y residuos radioactivos.
- Peligrosidad: Residuos tóxicos y peligrosos, inertes y no peligrosos.

La clasificación más utilizada corresponde al **origen de los residuos**, y se describe brevemente a continuación.

- Residuos industriales:

  Residuos resultantes de los procesos de fabricación, de transformación, de utilización, de consumo, de limpieza o mantenimiento generados por la actividad industrial, excluidas las emisiones a la atmósfera reguladas en la Ley 34/2007, de 15 de noviembre. Como ejemplo se consideran los residuos industriales inertes, los asimilables a urbanos y los residuos industriales especiales.
- Residuos agrícolas y ganaderos:

  Residuos que provienen de las actividades agrarias en sentido amplio. A su vez, estos residuos se dividen en tres tipos según la actividad en que se originen: residuos agrícolas, forestales y ganaderos.
- Residuos sanitarios:

  Son los residuos generados en cualquier actividad sanitaria, incluidos los desechos de actividades veterinarias, que pueden contener agentes patógenos y causar enfermedades en personas expuestas. Como ejemplo destacan los residuos químicos, los especiales radiactivos o especiales restos anatómicos de entidad.
- Residuos Urbanos:

  Son los residuos generados en los domicilios, en los núcleos urbanos o en zonas de influencia. Según la legislación 22/2011 de residuos y suelos contaminados, estos pueden ser clasificados en residuos domésticos y comerciales. Como residuos domésticos se entienden los “generados en los hogares como consecuencia de las actividades domésticas. Se consideran también residuos domésticos los similares a los anteriores generados en servicios e industrias”. Como residuos comerciales se entienden los “residuos generados por la actividad propia del comercio, al por mayor y al por menor, de los servicios de restauración y bares, de las oficinas, los animales domésticos muertos y los vehículos abandonados”.

- Biorresiduo:

  Según la Ley 22/2011 se define biorresiduo el “residuo biodegradable de jardines y parques, residuos alimenticios y de cocina procedentes de hogares, restaurantes, servicios de restauración colectiva y estabelecimientos de venta colectiva al por menor, así como, residuos comparables de plantas de procesado de alimentos.

Esta tesis se centra en el tratamiento de **residuos orgánicos biodegradables** de distintos orígenes (especificados en el Capítulo 3).

1.2.2. Aprovechamiento de residuos sólidos orgánicos

Se entiende por aprovechamiento el conjunto de fases sucesivas de un proceso en el que la materia inicial es un residuo. El procesamiento tiene el objetivo económico de valorizar el residuo u obtener un producto o subproducto utilizable.

La maximización del aprovechamiento de los residuos generados y en consecuencia la minimización del residuo contribuye a conservar y reducir la demanda de recursos naturales, disminuir el consumo de energía, reducir los costes, así como reducir la contaminación ambiental.

A continuación se presentan en términos generales las características principales de diversos tipos de tratamientos y/o valorización de residuos existentes en la actualidad.

a) Alimentación animal:

   Principalmente en las zonas rurales, la fracción orgánica de determinados residuos (especialmente agrícolas) se separa y se destina para la alimentación animal, en su mayoría ganado y cerdos.

b) Compostaje:

El proceso de compostaje constituye actualmente uno de los métodos de tratamiento de los residuos sólidos orgánicos más empleados, especialmente como alternativa de valorización o inertización de residuos contaminantes. Es un proceso aerobio, es decir en presencia de oxigeno, que permite la degradación bioquímica de la materia orgánica presente en los residuos. Esta degradación aerobia se realiza gracias a la acción de microorganismos presentes en el sustrato solido que transforma el residuo en un compuesto bioquímicamente estable denominado “compost”.

El proceso de compostaje se produce mediante el desarrollo de tres etapas, durante las cuales se consume la materia orgánica y a su vez se genera dióxido de carbono. Estas etapas son: *crecimiento* (de los microorganismos presentes en los residuos), *etapa termófila* (producción de la actividad bacteriana a 50-70ºC) y *etapa de maduración* (proceso de descomposición de la materia orgánica).

c) Biocombustibles:

Biocombustible es cualquier combustible líquido, sólido o gaseoso, procedente de la biomasa (materia orgánica proveniente de origen animal o vegetal). Este término incluye el bioetanol, metanol, biodiesel y el biogás, cuyo desarrollo actual está siendo exponencial.

d) Vertederos:

Consiste en un espacio confinado destinado a la deposición y descomposición de los residuos. Se trata de uno de los destinos habituales de los residuos sólidos junto con los lodos de depuradoras. De hecho, los lodos constituyen el residuo orgánico por excelencia de vertederos. Sin embargo, la deposición en vertederos tiene las limitaciones propias de estos sistemas de gestión. Es frecuente encontrar problemas de gases incontrolados, olores, lixiviados que pueden contaminar las aguas subterráneas, o situaciones sanitarias no deseadas.

e) Gasificación:

La gasificación consiste en un proceso termoquímico que permite transformar la materia orgánica presente en los residuos sólidos en un gas con un bajo poder calorífico. Este proceso consta de tres etapas o fases: secado, craqueo y gasificación. Este método de tratamiento presenta varias ventajas, entre las cuales están la facilidad de valorización del residuo dependiendo poco de su composición, buen rendimiento y bajo impacto ambiental colateral. Sin embargo su coste es elevado.

f) Pirolisis:

La pirolisis es un proceso de combustión que se produce en ausencia de oxigeno a altas temperaturas comprendidas entre los 550 y 1100ºC. Este tratamiento permite transformar la materia orgánica de un residuo solido y convertirlo en gases, líquidos o materiales de naturaleza inerte. Es una técnica frecuentemente usada en relación con la incineración.

g) Oxidación:

La oxidación consiste en un proceso donde se logra oxidar la materia orgánica en suspensión o disolución acuosa presente en los residuos, con la consecuente obtención de agua, dióxido de carbono y otros compuestos orgánicos simples. Las condiciones de operación son el empleo de agentes oxidantes, oxigeno atmosférico a presión y temperaturas de 300ºC aproximadamente, por lo que resulta una tecnología altamente costosa.

h) Digestión anaerobia:

Es un proceso biológico de conversión de la materia orgánica en substancias inocuas y gases, como metano y dióxido de carbono mediante condiciones anaerobias (ausencia de oxigeno).

Atendiendo a las directivas, Europea (1999/31/CE) y nacional (Real Decreto 1481/2001), la digestión anaerobia se presenta como un **proceso enormemente atractivo**, ya que utiliza materia orgánica biodegradable como materia prima, produciendo un residuo (con excelentes características para ser utilizado como fertilizante para el suelo) y biogás con alto contenido en metano (aprovechable como fuente de energía térmica o eléctrica mediante sistemas de cogeneración).

1.3. Revisión del estado del arte sobre energía y normativa

1.3.1. Energía en España

En la civilización moderna, la disponibilidad de energía está fuertemente ligada al nivel de bienestar, a la salud y a la esperanza de vida del ser humano. En la sociedad actual, los países más pobres muestran los consumos más bajos de energía, mientras que los países más ricos utilizan grandes cantidades de la misma. Sin embargo este escenario está cambiando de forma drástica, cambio que se acentuará en los próximos años, donde serán precisamente los países en vías de desarrollo quienes experimenten con mayor rapidez un aumento en su consumo de energía debido al incremento que tendrán tanto en sus poblaciones como en sus economías.

Se prevé que el consumo de energía en el mundo se incremente en un 57% entre 2004 y 2030, a pesar de que se espera que el aumento de precios tanto del petróleo como del gas natural siga en aumento. Se prevé que el consumo de energía en el mercado experimente un incremento medio de un 2,5% por año hasta 2030 en los países ajenos a la OCDE, mientras que en los países miembros será tan solo del 0,6%; así, durante este periodo, los países OCDE incrementarán su demanda energética en un 24%, mientras que el resto de países lo harán al 95%.

Los datos oficiales de 2011 señalan un consumo total de energía en España de 130.2 millones de toneladas equivalentes de petróleo (Tep), cantidad muy similar a los años anteriores.

El consumo de energía primaria en este año ha estado afectado por el bajo perfil de la actividad económica y por un clima benigno durante todo el año.

Los rasgos más significativos del comportamiento de las fuentes de energía en 2011 frente al 2010 son:

- Aumento del consumo de carbón (+82%), principalmente del carbón de importación.
- Decrece (-3,3%) el consumo de petróleo y por tanto de los productos petrolíferos, consecuencia de las bajadas en prácticamente todos sus usos finales.
- Disminuye el consumo de gas natural en un 7%, debido principalmente al descenso de la demanda de los ciclos y suavidad de las temperaturas invernales.
- Caída de la generación nuclear (-7%), consecuencia de un mayor régimen de paradas técnicas.
- Caída de la producción del conjunto de las energías renovables (-3,5%). Han registrado descensos las producciones de hidráulica, eólica, biomasa y residuos. Han crecido geotérmica y, especialmente, la solar, con una avance estimado del 62%.

A continuación se presenta una tabla del consumo de energía primaria en España en los años 2008-2011, incluidas todas las renovables, según fuente de la Secretaria de Estado de Energía, Ministerio de Industria, Energía y Turismo.

Tabla 1.1 – Consumo de energía primaria en España

	2008		**2009**		**2010**		**2011**	
	KTep	%	KTep	%	KTep	%	KTep	%
Carbón	13983	9.8	10353	7.9	7156	5.5	13045	10.0
Petróleo	68182	47.9	63673	48.8	60993	46.9	58957	45.3
Gas Natural	34782	24.4	31104	23.8	31182	24.0	28992	22.3
Nuclear	15368	10.8	13750	10.5	16155	12.4	15029	11.5

Energías Renovables:	10942	7.7	12325	9.4	15263	11.7	14727	11.3
- Hidráulica	2004	1.4	2253	1.7	3636	2.8	3625	2.0
- Eólica	2795	2.0	3196	2.4	3798	2.9	3617	2.8
- Biomasa y Residuos	5162	3.6	5087	3.9	5380	4.1	5235	4.0
- Biocarburantes	620	0.4	1058	0.8	1413	1.1	1579	1.2
- Geotérmica	8	0.0	9	0.0	16	0.0	21	0.0
- Solar	353	0.2	718	0.6	1020	0.8	1650	1.3
Total	142308	100.0	130508	100.0	130032	100.0	130225	100.0

1.3.2. Plan de Energías Renovables en España

España mantiene desde hace años un notorio crecimiento en la demanda energética. La creciente y excesiva dependencia energética exterior (alrededor del 80% en los últimos años) y la necesidad de preservar el medio ambiente, obligan al fomento de formulas eficaces para un uso eficiente de la energía y la utilización de fuentes limpias. Por tanto, el crecimiento sustancial de las fuentes renovables, junto a una importante mejora de la eficiencia energética, responde a motivos de estrategia económica, social y medioambiental.

El Plan de Acción Nacional de Energías Renovables 2011-2020 se encuentra actualmente en proceso de elaboración, por lo que tanto el escenario como los objetivos que se mantienen son los marcados por el plan anterior, Plan de Energías Renovables 2005-2010 (PER).

Para la formación del escenario del mapa energético en 2020, se ha tenido en cuenta la evolución del consumo energético en España, el alza de los precios del petróleo en relación a los mismos en la década de los noventa y la intensificación sustancial de los planes de ahorro y eficiencia energética. Las conclusiones principales del informe se enumeran a continuación:

- En una primera estimación, la aportación de las energías renovables al consumo final bruto de energía sería del 22.7% en 2020 – frente a un objetivo para España del 20% en 2020 – equivalente a unos excedentes de energía renovable de aproximadamente de 2.7 millones de toneladas equivalentes de petróleo (Tep).
- Como estimación intermedia, se consideró que en el año 2012 la participación de las energías renovables fuera del 15.5% (frente al valor orientativo previsto en la trayectoria indicativa del 11.0%) y en 2016 sea del 18.8% (frente al 13.8% previsto en la trayectoria).
- El mayor desarrollo de las fuentes renovables en España corresponde a las áreas de generación eléctrica, con una previsión de la contribución de las energías renovables a la generación bruta de electricidad del 42.3% en 2020.

El principal objetivo del plan 2011-2020 consiste en alcanzar **al menos un 20% de obtención de energía de fuentes renovables, respecto al consumo final de energía antes del 2020**, llegando a una contribución de las fuentes renovables al sector del transporte de un 10% como mínimo ese mismo año.

Cuando concluya el PER 2011-2020, se calcula que la energía eólica seguirá siendo la energía renovable que más aporte, seguida de la energía solar. Entretanto, la procedente de la biomasa, el biogás y los residuos verá incrementada su contribución al suministro eléctrico.

El PER 2005-2010, plan actualmente en vigor, propone un análisis de objetivos por áreas técnicas, es decir, para cada una de las energías renovables: eólica, hidroeléctrica, solar, térmica, solar fotovoltaica, biomasa y biogás.

Aunque los objetivos fijados en su día por el plan para el área del **biogás** fueran modestos, durante los últimos años su crecimiento ha sido muy superior al inicialmente previsto.

De acuerdo con la evolución registrada hasta la fecha y con los análisis llevados a cabo para la elaboración del PER 2005-2010, el objetivo establecido para el área supone un incremento de la potencia instalada durante este periodo de 94 MW, con una producción de electricidad asociada a ese incremento que asciende en 2010 a 592 GWh, y se traduce, en términos de energía primaria en 188 KTep adicionales.

En la tabla siguiente, se recogen los **objetivos energéticos propuestos por el tipo de residuo para la producción de biogás**, según el PER.

Tabla 1.2. Tipo de residuo empleado según el PER 2005-2010

PER 2005-2010	
Recursos (Tep)	
Residuos ganaderos	8000
Fracción orgánica de residuos solidos	110000
Residuos industriales biodegradables	40000
Lodos de depuradora	30000
Aplicaciones (Tep)	
Aplicaciones eléctricas	188000

Cabe señalar con respecto al biogás que España cuenta con amplia experiencia en el desarrollo de instalaciones de aprovechamiento energético del biogás producido tanto en instalaciones de desgasificación de vertederos como en el tratamiento de residuos biodegradables de origen industrial o de lodos de depuradoras.

En la fase de desarrollo actual de este tipo de aplicaciones, los objetivos a alcanzar dentro del capítulo de innovación tecnológica deberían ser:

- Mejora de eficiencia en los procesos de producción, depuración y limpieza de biogás.
- Desarrollo de sistemas de codigestión de los residuos biodegradables.
- Desarrollo de sistemas para la inyección de biogás en la red de gas natural.
- **Avances tecnológicos ligados al empleo de pequeñas cantidades de residuo (ganadero, industrial o de lodos de depuradora) para el aprovechamiento energético del biogás producido en su digestión anaerobia**.

1.3.3. Plan Nacional Integrado de Residuos (2008-2015) - PNIR

De la mala gestión de los residuos se pueden derivar efectos colaterales dañinos para la mayoría de los medios receptores: de los residuos orgánicos biodegradables se puede generar amoníaco y metano; si se trata de sustancias tóxicas, persistentes a bioacumulativas, pueden contaminar los suelos, las aguas e, incluso, el aire; el vertido incontrolado de muchos otros residuos especiales conlleva daños tales como la contaminación de las aguas y el suelo, riesgos a la salud pública, entre otros.

Si a esto añadimos el fenómeno, generalizado en todos los países avanzados, del incremento paulatino y hasta ahora imparable del aumento en la generación de residuos, se llega a la conclusión de la necesidad de regularlos con rigor ecológico y planificar la puesta en práctica de esa regulación de manera nacional y realista.

En la actual directiva marco europea, Directiva 2006/12/CE, y en todas sus antecesoras jurídicas, se pone de manifiesto esta necesidad; de ellas se deriva la obligación de los estados miembros de dotarse de estos instrumentos jurídicos y de planificación. También en la actual Estrategia Comunitaria de Gestión de Residuos, se contempla la conveniencia de elaborar planes de residuos.

En la Ley 10/1998, de Residuos, artículos 5 y 6, se establece la obligación de elaborar y aprobar Planes Nacionales de Residuos, que se confeccionarán por integración de los respectivos planes autonómicos. En los Planes Nacionales deben figurar objetivos de reducción, reutilización, reciclaje, otras formas de valorización, y eliminación, así como los medios para conseguirlos, el sistema de financiación y el procedimiento de revisión.

Descripción general del PNIR

Para mejorar la gestión de todos los residuos generados en España, estimular a las distintas administraciones y agentes involucrados hacia el logro de objetivos ecológicos ambiciosos, y dar cumplimiento a las normas legales citadas, se ha adoptado el Plan Nacional Integrado de Residuos (PNIR), en el que se incluyen, en forma de anexos, 13 planes de residuos específicos en cada uno de los cuales se establecen medidas concretas y objetivos ambientales.

En el plan se incluyen todos los residuos que figuran en la Lista Europea de Residuos (LER), generados en España o procedentes de países extranjeros, excepto los siguientes:

- Los residuos radioactivos, regulados por la Ley 25/1964, de 29 de Abril de energía Nuclear.
- Los residuos de origen animal regulados en el Reglamento (CE) nº 1774/2002 del parlamento Europeo y del consejo, de 3 de Octubre de 2002, por el que se establecen las normas sanitarias aplicables a los subproductos animales no destinados al consumo humano.

Objetivos del PNIR 2008-2015

Los objetivos generales del plan se concretan en los siguientes puntos:

- Modificar la tendencia actual del crecimiento de la generación de residuos.
- Erradicar el vertido ilegal.
- Disminuir el vertido y fomentar de forma eficaz: la prevención y la reutilización, el reciclado de la fracción reciclable, así como otras formas de **valorización de la fracción de residuos no reciclable.**
- Completar las infraestructuras de tratamiento y mejorar el funcionamiento de las instalaciones existentes.
- Obtener estadísticas fiables en materia de infraestructuras, empresas gestoras y producción y gestión de residuos.

Principios rectores del PNIR

Constituye un hecho el que cada vez se abran más posibilidades para el segundo uso de materiales procedentes de los residuos, gracias al avance tecnológico, verdaderamente incesante en los últimos años en este campo. Esta circunstancia obliga a establecer directrices para la selección de la mejor opción de gestión posible para los diferentes residuos, ya que es evidente la imposibilidad de hacer análisis de impacto específicos para cada residuo y en cada circunstancia concreta. Este es el origen del **principio de jerarquía**, consistente en una secuencia ordenada de modalidades de gestión, de mayor a menor calidad ecológica, que se acepta como directriz general a la hora de decidir o escoger la mejor gestión para los residuos. Este principio sólo es aplicable cuando hay más de una opción de gestión posible, entendiendo este término como su viabilidad técnica y económica.

En la Ley española de residuos, se adoptó el **principio de jerarquía** de 5 niveles y por el orden: prevención, reutilización, reciclaje, valorización energética y eliminación (vertedero, incineración sin recuperación energética o con baja recuperación energética). En las normas actualmente vigentes en la UE se incluye este principio, pero no se especifica claramente la prioridad de la reutilización sobre el reciclaje.

El principio de jerarquía es necesario, por múltiples razones. La experiencia acumulada a lo largo de los últimos decenios, los datos empíricos disponibles, la mayoría de los estudios disponibles de impacto ambiental comparativos entre modalidades de gestión, ponen de manifestó que el orden establecido en el principio de jerarquía de 5 niveles está justificado. No se trata de hacer de ese principio algo absoluto, justificado en el 100% de los casos; pueden hacerse excepciones, pero éstas tienen que estar justificadas y apoyadas en análisis de impactos y de ciclos de vida con los que se demuestre que se obtiene un beneficio ecológico invirtiendo, en algún caso, esta ordenación; y en estos casos, parece lógico requerir esas pruebas a quienes pretendan alterar o invertir el orden general del principio.

Capítulo 2

Justificación del trabajo y objetivo global

2.1. Justificación del trabajo

2.1.1. Primer punto de vista: Necesidad de tratamiento de los residuos orgánicos

Según el artículo 5 del **Real Decreto 1481/2001**, de 27 de diciembre, por el que se regula la eliminación de residuos mediante deposito en vertedero, la Administración General del Estado y las Comunidades Autonómicas deben elaborar un programa conjunto de actuaciones para reducir los residuos biodegradables destinados a vertedero. Este programa debe incluir medidas que permitan alcanzar los objetivos específicos que para residuos urbanos biodegradables recoge el artículo 5.2 del citado Real Decreto, en particular mediante reciclaje, compostaje y otras formas de valorización como **producción de biogás mediante digestión anaerobia**.

El artículo 5.2 del Real Decreto 1481/2001 establece que se deberá alcanzar el siguiente objetivo: "A más tardar el 16 de julio de 2016, la cantidad total (en peso) de residuos urbanos biodegradables destinados a vertedero no superará el 35% de la cantidad total de residuos urbanos biodegradables generados en 1995."

Otro tipo de residuos que también considera el Plan Nacional de Residuos Urbanos, son los lodos de depuradora cuya producción va en aumento debido al crecimiento en el número de EDARs, consecuencia directa de la puesta en práctica de la Directiva Europea de Tratamiento de Aguas Residuales Urbanas (directiva 91/271/CEE), y del aumento en el nivel de tratamiento del agua. Esta directiva fija el nivel de rendimiento de depuración adecuado según las circunstancias (básicamente, las dimensiones del núcleo urbano y la categoría de los puntos de vertido.

Tanto el **Plan Nacional de Lodos de Depuradora de Aguas Residuales** (2008-2015) como el **Plan de Residuos PNIR**, recogen entre sus objetivos **la valorización energética de los lodos de depuradoras y de los residuos biodegradables.**

2.1.2. Segundo punto de vista: Los residuos como recurso

Actualmente los recursos energéticos convencionales van siendo más escasos, por lo que se hace necesario utilizar las energías renovables de forma tecnológicamente correcta, entre ellas, el biogás, obtenido de la digestión anaerobia.

El proceso de generación conjunta de electricidad y calor, representa una oportunidad medioambiental y tecnológicamente atrayente para **aprovechar el biogás obtenido a partir de la digestión de residuos**, creando fuentes energéticas alternativas, dando así un paso importante para reducir el calentamiento global y su efecto invernadero, que provoca cambios climáticos incalculables y a menudo devastadores.

Como muestra la tabla 1.2 anteriormente presentada, en el PER 2005-2010 existe una declaración de objetivos para la producción de biogás a partir de distintos residuos biodegradables concretos.

2.2. Objetivo global

Teniendo en cuenta lo anteriormente expuesto, el presente trabajo fija como **objetivo general la OPTIMIZACIÓN DE LA DIGESTIÓN ANAEROBIA DE DISTINTOS RESIDUOS SÓLIDOS ORGÁNICOS**, de modo que se cumplan los objetivos energéticos y medioambientales marcados por la legislación y los planes vigentes en España relativos a:

1- Disminución de la cantidad de residuos biodegradables destinados a vertedero.
2- Valorización energética de los lodos de depuradora y de los residuos biodegradables.
3- Aumento en la generación de energía renovable, en concreto en el área del biogás procedente de digestión anaerobia.

Capítulo 3

Antecedentes Específicos

3.1. Planteamiento de la investigación bibliográfica realizada

Una vez fijado el objetivo global de optimización de la digestión anaerobia de distintos tipos de residuos, surgen una serie de interrogantes que llevan a realizar una **investigación bibliográfica específica previa al desarrollo experimental de la tesis**:

1- Primer interrogante: ¿Qué residuos seleccionar para la tesis?
2- Segundo interrogante: ¿Hay alguna limitación en la digestión anaerobia de residuos sólidos?
3- Tercer interrogante: ¿Qué alternativas de optimización de la digestión anaerobia?
4- Cuarto interrogante: ¿Qué alternativa de mejora de la digestión anaerobia de residuos sólidos orgánicos es seleccionada para el presente estudio?

Dichos interrogantes corresponden a los apartados 3.2, 3.3, 3.4 y 3.5.

3.2. Selección de los residuos sólidos orgánicos de trabajo

Tomando como enfoque principal el objetivo global indicado relativo a la optimización de la digestión anaerobia de residuos sólidos urbanos, la primera pregunta que surge al empezar el trabajo es: **¿Qué residuos se seleccionan?**

Una primera revisión de los distintos residuos potencialmente metanizables conduce a la tabla 3.1.

Manteniendo la clasificación según el origen de los residuos presentada en el capítulo 1, se consideran cuatro orígenes principales: industrias agroalimentarias, agrícolas y ganaderos, urbanos y otros residuos industriales.

Tabla 3.1 – Residuos orgánicos potencialmente metanizables

Residuos de Industrias Alimentarias	**Residuos Agrícolas y Ganadero**	**Residuos Urbanos**	**Residuos Industriales**
Conservas	Ganado porcino, vacuno, caprino y avícula	Lodos de EDAR	Biodiesel, Bioetanol
Zumos, cerveza y otras bebidas	Paja	Fracción orgánica de residuos sólidos urbanos	Farmacéutica
Lácteas Cárnicas, Pescado	Residuos agrícolas		Bioquímica Algas

Siendo imposible plantear una tesis que abarque todos los residuos, el punto de partida fue la selección de los residuos en los que enfocar el estudio concreto de la tesis.

Se decidió seleccionar al menos un residuo de cada tipo, priorizando aquellos que resultan más representativos en el panorama español.

Con este planteamiento, los residuos seleccionados para el desarrollo experimental de la tesis fueran:

1- Residuos industriales: **Cáscara de naranja** de la industria de elaboración de zumos, y **bagazo de cerveza** de la industria cervecera. Ambas industrias tienen un elevado volumen de producción en España.
2- Residuo agrícola: **Paja de trigo**, por ser el cereal de mayor producción.
3- Residuo ganadero: **Purín de cerdo**, que es el residuo ganadero más abundante en España.
4- Residuo urbano: **Lodos de depuradora**, cuya crecente producción y problemática ha sido descrita en el capítulo 1.

A pesar de considerar de gran interés los residuos sólidos urbanos (por su elevada producción) y las algas (por su creciente desarrollo y generación), ambos residuos son la materia prima de estudio en sendas tesis relativas a su digestión anaerobia, actualmente en curso en el departamento de Ingeniería Química y Tecnología del Medio Ambiente de esta universidad. Por ello en la presente tesis no han sido consideradas.

A continuación se describe en concreto para cada uno de los residuos seleccionados la situación en España relativa a su generación y destino.

1. Cáscara de naranja y bagazo de cerveza

a) Cáscara de naranja

Generación: España es considerada el sexto productor mundial de zumos. Actualmente, las naranjas son los frutos de mayor producción a escala mundial, fundamentalmente en la comunidad Valenciana donde se producen en torno a 5.7 millones de toneladas y se exportan más del 80% del total nacional.

Destino: La cáscara se destina fundamentalmente a la fabricación de piensos compuestos de ganado. Como alternativa de valorización económica se emplean en la industria cosmética y en el sector farmacéutico para generar productos de valor añadido.

b) Bagazo de cerveza

Generación: En España se producen en media cerca de 2.600 millones de litros de cerveza al año. En su elaboración se genera una serie de subproductos o residuos, siendo el bagazo uno de los residuos sólidos mayoritario en esta industria.

El bagazo es un residuo de la etapa de cocción, en lo que se elabora el mosto de cerveza con el empleo de malta de cereales después de la solubilización de los almidones.

Destino: Su uso principal es como alimento para la ganadería, si bien en muchas ocasiones se depositan en vertedero.

2. Paja de trigo

Generación: En España se generan unos 27 millones de toneladas de residuos de cultivos agrícolas. La paja de trigo es un subproducto fibroso altamente disponible, aunque su utilización en alimentación animal está limitada por su bajo valor nutricional.
La cantidad de paja de trigo generada en Castilla y León en el año 2009 fue de 259.102 ton/año.
Destino (de mayor a menor significancia): Alimentación animal, camas para ganado, biocombustibles, compostaje, fertilizante natural, valorización energética por incineración.

3. Purines de cerdo

Generación: Los residuos ganaderos son todas aquellas fracciones sólidas y/o liquidas excretadas por los animales consecuencia de la actividad biológica. La problemática de su generación viene asociada a la producción en régimen intensivo o semi-intensivo. Las granjas de explotación intensiva de ganado porcino producen un residuo ganadero líquido, denominado de purín, que presenta una elevada carga orgánica y contenido en nutrientes (N e P principalmente) y exige un tratamiento adecuado para evitar daños medioambientales y a la salud.
La cantidad generada en Castilla y León en el año de 2009 fue de 2.522.945 ton/año.
Destino: Compostaje y posterior aplicación agrícola o valorización energética vía incineración.

4. Lodos de depuradora

Generación: Los lodos generados durante la depuración de las aguas residuales se tratan generalmente mediante digestión anaerobia en la propia depuradora, y tras una etapa de deshidratación o secado, se convierten en un residuo a evacuar de la EDAR.
El volumen de lodos de depuradora generados en el año de 2005 fue del orden de 1.300.000 toneladas de materia seca.
Destino: Aplicación en agricultura vía compostaje si bien en muchas ocasiones se destinan a vertedero controlado.

3.3. Digestión anaerobia de residuos sólidos

Como se ha puesto de manifiesto en el Capítulo 1 de "Antecedentes generales", los residuos orgánicos son problemáticos ya que se generan en grandes cantidades, tienen una alta humedad y son fácilmente putrescibles, por lo que la nueva normativa medioambiental ha reducido drásticamente su deposición en vertederos. La opción de valorización energética mediante **obtención de biogás por digestión anaerobia** permite **transformar un problema en una oportunidad**, con las siguientes ventajas:

- El residuo fermentado está más estabilizado que el material original, pudiendo ser utilizado para diversos usos, con o sin tratamiento posterior (aplicación directa al suelo, compostaje, abono, etc.).
- La humedad no es un problema en la producción de biogás; se pueden tratar distintos residuos conjuntamente, reduce el problema de olores, etc.
- Utilización del biogás como combustible para calderas y motores de cogeneración o para calefacción.
- Rendimientos económicos atípicos: ingresos adicionales por gestión de residuos de terceros, venta de abonos orgánicos, ahorro en energía (eléctrica y térmica), acceso a subvenciones por tratarse de una energía renovable.

Finalmente, esta vía resulta muy atractiva a corto plazo debido al escenario político y económico favorable a las energías renovables.
Las situaciones en que se están aplicando son las siguientes:

- Aprovechamiento energético del biogás producido en plantas de depuración anaerobia de aguas residuales de elevada carga orgánica (cerveceras, azucareras, mataderos, etc.).
- Tratamiento de residuos ganaderos (purines, estiércol, gallinaza) con producción y aprovechamiento de biogás para su uso en granja.
- Digestión anaerobia de distintos residuos orgánicos de origen agroalimentario (hortofrutícolas, agrícolas, grasa, etc.) para la producción y aprovechamiento del biogás generado.

- Obtención de abonos orgánicos (sólidos o líquidos) de alto valor añadido, a partir del producto resultante de la digestión anaerobia donde se produce biogás.
- Utilización del biogás en el secado y estabilización de residuos orgánicos agroalimentarios de alta humedad, para facilitar su gestión.

3.3.1. Mecanismo del proceso de digestión

El proceso de digestión anaerobia consiste en una cadena secuencial de rutas metabólicas y acciones de los diferentes grupos tróficos de bacterias anaerobias, que participan en la conversión de la materia orgánica compleja en metano y dióxido de carbono. Debido a la complejidad del proceso, es esencial que exista una relación equilibrada y coordinada entre los distintos grupos de bacterias presentes.

La figura 3.1 presenta un esquema típico del proceso de digestión anaerobia, siendo posible distinguir al menos **4 secuencias principales de degradación**; [1]hidrólisis, [2]acidogénesis o fermentación, [3,4]acetogénesis y [5]metanogénesis.

La etapa de **hidrólisis** constituye el primer paso de la degradación anaerobia. Es la conversión de los bio-polímeros (proteínas, carbohidratos y grasas) en sus monómeros (aminoácidos, azúcares y ácidos grasos de cadena larga, respectivamente), por enzimas extracelulares producidas por bacterias hidrolíticas facultativas o estrictamente anaerobias (Chandra et al. 2012). Es normalmente un proceso lento, siendo, en general, las grasas hidrolizadas más lentamente que las otras moléculas. La velocidad de degradación está afectada por un gran número de factores, destacando que, grandes partículas con baja superficie específica son generalmente hidrolizadas, y muchas veces la materia orgánica puede estar encapsulada en fibras (difícilmente degradable). Por las razones anteriores, <u>la etapa de hidrólisis es considerada como la etapa limitante del proceso para residuos sólidos</u> (Appels et al. 2008). Hartmann et al. (2000) han estimado que cerca de 25% de la materia orgánica no es digerida por no estar bio-disponible para las bacterias.

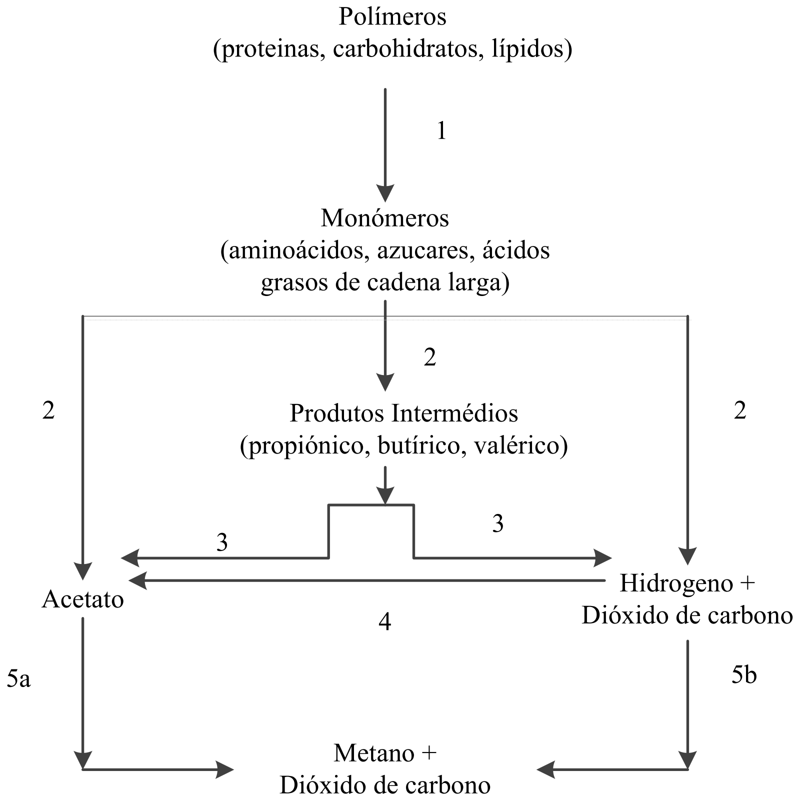

Figura 3.1 – Esquema de reacciones del proceso de digestión anaerobia. 1 - Hidrólisis; 2 – Acidogénesis; 3 – Acetogénesis sintrófica; 4 – Homoacetogénesis; 5a - Metanogénesis acetotrófica; 5b – Metanogénesis Hidrogenotrófica. Adaptado de (Metcalf et al. 2003)

En la etapa siguiente, **acidogénesis** o **fermentación**, los productos de la hidrólisis son transportados al interior de la célula, donde se transforman en acetato, productos intermedios (ácidos grasos volátiles, alcoholes) e hidrógeno. La población de microorganismos acidogénicos representa 90% de la población bacteriana total de los digestores anaerobios, presentando reducidos tiempos de degradación; por tanto, esta etapa nunca será limitante del proceso. En esta fase, el hidrógeno tiene un papel preponderante en la distribución de los productos del proceso. En ella se verifica la disminución del pH del medio por la liberación de protones. Cuando la presión parcial del hidrógeno es inferior a 10^{-4} atm se forma, mayoritariamente, acetato e hidrógeno; siendo este proceso metabólico más rentable en términos energéticos (Mosey et al., 1984).

La tercera etapa, la de **acetogénesis**, consiste en la transformación de los productos de la fermentación en acetato, dióxido de carbono e hidrógeno por la acción de las bacterias homoacetogénicas y de las bacterias sintróficas o productoras de hidrógeno (OHPA).

Como etapa final del proceso de digestión anaerobia ocurre la **metanogénesis**. En esta etapa se produce metano a partir de acético o hidrógeno y dióxido de carbono. Siendo el acético el principal precursor del metano (70% del metano proviene del acético) resulta evidente la importancia de esta conversión en todo el conjunto de las etapas de la digestión anaerobia. Las bacterias implicadas en la metanogénesis son, generalmente, divididas en dos grupos: bacterias hidrogenotróficas (*hydrogenotrophic arhae*) y acetoclásticas (*aceticlastic methanogens*). Las primeras controlan el potencial redox del medio, manteniendo la concentración de hidrógeno en niveles bajos, usando el hidrógeno como dador de electrones y el dióxido de carbono como aceptador. Las bacterias acetoclásticas son responsables de la degradación del acetato, que es el principal precursor de metano.

3.3.2. Parámetros que influyen en la digestión anaerobia

Existe un número diversificado de parámetros influyentes para que las bacterias anaerobias puedan degradar la biomasa, bien relativos a la alimentación, o bien a las condiciones de operación en el interior del reactor. Es necesario controlar los parámetros de operación de modo que se logre operar en condiciones favorables para los microorganismos y así alcanzar rendimientos óptimos de depuración.

A continuación se explican algunos de los parámetros clave en el proceso de biometanización.

- Tiempo de retención: Se refiere al tiempo medio que los sólidos (SRT) permanecen en el reactor. Estos tiempos suelen variar entre 20-30 días dependiendo del tipo de materia orgánica a degradar. Generalmente elevados tiempos de retención originan además de una mayor acumulación de biogás, una reducción más eficaz de los sólidos totales en el reactor (de la Rubia et al. 2006), resultando como inconveniente un mayor volumen requerido del reactor.

- Temperatura: Pequeñas variaciones de temperatura afectan de modo importante a la actividad de las bacterias anaerobias y todo el desarrollo del proceso metabólico pudiendo incluso provocar inhibiciones (Weiland, 2010). Según la temperatura a que se lleve a cabo la digestión, se consideran tres rangos de temperatura: psicrófilo (<20ºC), mesófilo (25-40ºC) y termófilo (>45ºC), siendo los más usuales el mesófilo con temperaturas entre 30-38ºC y el termófilo con temperaturas entre 50-57ºC, en el cual la actividad de las bacterias anaerobias es máxima, si bien también son más sensibles a los cambios en el proceso.

- pH y capacidad *buffer*: El proceso de biometanización es largamente influenciado por los cambios de pH, siendo el rango 6.5-8.5 el más conveniente para evitar inhibiciones (Weiland, 2003). El valor del pH aumenta por la acumulación de amonio durante la degradación de las proteínas, mientras que con la acumulación de AGVs (ácidos grasos volátiles) resultantes de la degradación de la materia orgánica el valor del pH disminuye; considerándose un pH toxico para las metanogénicas cuando se encuentra por debajo del 6.6. En medios acuosos se usan el H_2CO_3, HCO_3^-, CO_3^{2-} como principal sistema *buffer*, que tiene como principal función neutralizar posibles cambios en el pH del medio.

- Relación C/N: El rango de 25-30 es considerado como óptimo para la digestión anaerobia (Chandra et al. 2012 a; Yadav et al. 2004). Una relación C/N elevada puede provocar la limitación de nitrógeno, compuesto este necesario para el crecimiento de las bacterias. De otra forma, relaciones bajas pueden provocar la inhibición de las bacterias por elevadas concentraciones de amonio.

3.3.3. Limitación para la digestión anaerobia de residuos sólidos: Necesidad de pre-tratamiento

Atendiendo a su naturaleza, se describe por separado la situación para lodos de depuradora y para residuos lignocelulósicos.

Lodos de depuradora

Dado que en el futuro cualquier aplicación del lodo al terreno exige la estabilización como una etapa imprescindible en el tratamiento, la tecnología de digestión anaerobia se convierte en una necesidad.

Esta tecnología se presenta como favorita frente a otras alternativas existentes (estabilización con cal o digestión aerobia); típicamente, entre 30 y 70% del lodo que se produce es tratado mediante digestión anaerobia, dependiendo de la normativa nacional y de las prioridades.

Los principales **beneficios** de la digestión anaerobia de lodos son los siguientes:

- Reducción del volumen de sólidos.
- Producción de energía en forma de biogás.
- Aumento en la calidad del lodo: Se consigue la inactivación de los patógenos (dependiendo de la temperatura y configuración del proceso).
- Estabilización del lodo: Se garantiza que el producto final pueda ser almacenado y manejado sin generar problemas de olores, dado que ya no es putrescible.

Sin embargo, su digestión anaerobia presenta una **limitación**: la velocidad de degradación es lenta debido a la baja solubilización de la materia orgánica suspendida y los sólidos orgánicos, que conduce a que la **etapa de hidrólisis** se convierta en **limitante**, disminuyendo la eficacia del proceso.

Los procesos de pre-tratamiento previo a la digestión anaerobia del lodo son un tema de creciente interés. Mediante un pre-tratamiento eficaz, se puede hacer el sustrato más accesible a las bacterias anaerobias, acelerando el proceso de digestión (aumento en la producción de metano), y disminuyendo consecuentemente la cantidad de lodo a depositar. Otras ventajas adicionales son (dependiendo del pre-tratamiento): la mejora de la deshidratabilidad del lodo, reducción de patógenos, o eliminación de espumas.

Biomasa lignocelulósica

La biomasa lignocelulósica (ejemplos: residuos agrícolas y ganaderos, determinados residuos de la industria agroalimentaria) tiene por constitución tres polímeros distintos: lignina, hemicelulosa y celulosa, en porcentajes distintas pero con una compactación de la materia orgánica elevada (por la presencia de la lignina) que puede dificultar el acceso de las bacterias para su descomposición.

Mientras la celulosa tiene una forma rígida y cristalina, la hemicelulosa tiene bajo peso molecular y cadenas laterales cortas, lo que le convierte en un polímero fácilmente hidrolizable. El tercer componente, lignina, tiene una compleja estructura molecular que confiere propiedades rígidas a la biomasa lignocelulósica (Naik et al. 2010).

De esta forma, y siendo la **hidrólisis** una de las **etapas limitantes del proceso**, es recomendable el empleo de pre-tratamientos de forma a favorecer la solubilización de la materia orgánica en el medio (Figura 3.2), facilitando el acceso de las bacterias.

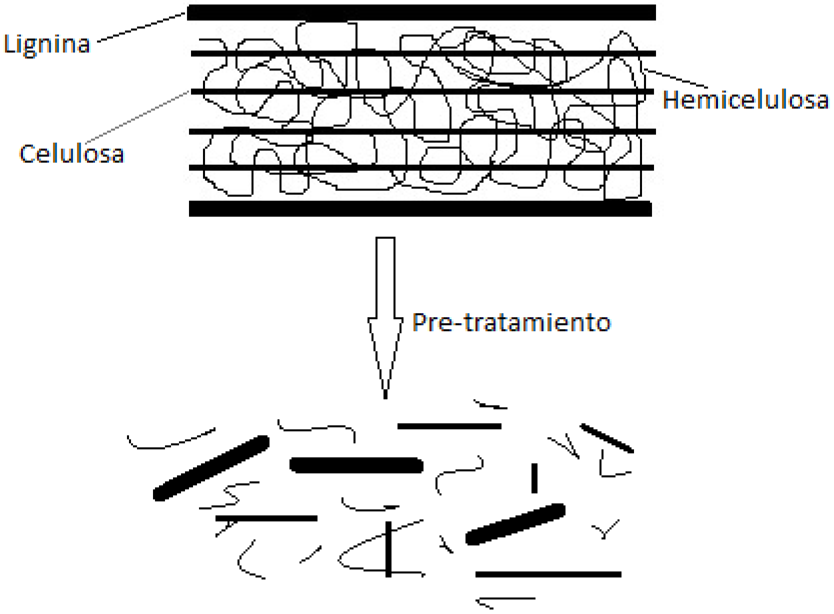

Figura 3.2. – Esquema de la estructura de la biomasa lignocelulósica antes y después del pre-tratamiento.

3.4. Alternativas de pre-tratamiento de residuos sólidos orgánicos como etapa previa a su digestión anaerobia

La selección de un pre-tratamiento depende de distintos factores tales como la efectividad del pre-tratamiento o la relación al coste económico. Los principales efectos que se buscan con un pre-tratamiento son: reducción del tamaño de partícula, solubilización, incremento en la biodegradabilidad y disminución de volumen del residuo.

3.4.1. Alternativas de pre-tratamiento de lodos de depuradora

La investigación y desarrollo de procesos de pre-tratamiento previo a la digestión anaerobia nació para el tratamiento de lodos de depuradora, de modo que toda la información que se presente en este apartado corresponde a este campo.

Las distintas tecnologías de pre-tratamiento que se han desarrollado se pueden clasificar en A) mecánicos o físicos, B) químicos y físico-químicos, C) biológicos. A continuación se describen brevemente los distintos procesos.

A) Pre-tratamientos mecánicos y físicos: Proceso de molienda, irradiación y térmicos.

A1) Molienda – Molino de Bolas

Este dispositivo consiste en una cámara de molienda cilíndrica (de hasta 1 m^3 de volumen) llena casi por completo de bolas, a las que se induce un movimiento rotativo por medio de un agitador.

La desintegración de los microorganismos se da debido a las fuerzas de rozamiento y presión entre las bolas.

El proceso de molienda es más eficaz para lodo activado con proceso de aeración (24% de incremento) que para lodo activado con tiempos de retención elevados (Baier et al. 1997; Kopp et al. 1997).

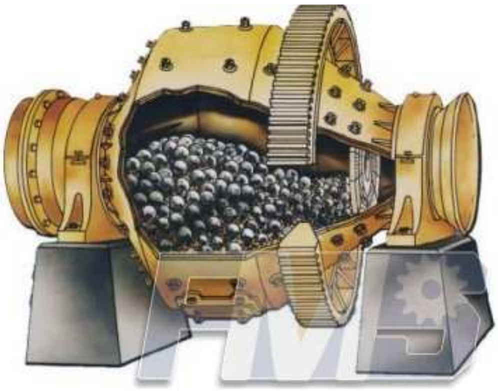

Figura 3.3. – Ejemplo de un molino de bolas

A2) <u>Homogeneizadores de alta presión</u>

Estas unidades se componen de una bomba de alta presión multi-etapa y una válvula de homogeneización. La bomba comprime la suspensión de lodo hasta presiones de centenas de bares, pudiendo llegar hasta los 900 bares (Muller et al. 1998). Cuando dicha suspensión pasa a través de la válvula, la presión disminuye por debajo de la presión de vapor del fluido.

Este proceso fue testado a la escala real, obteniendo-se un incremento en la producción de biogás hasta unos 30% y reducción del volumen de lodo de 23% (Onyeche et al. 2007).

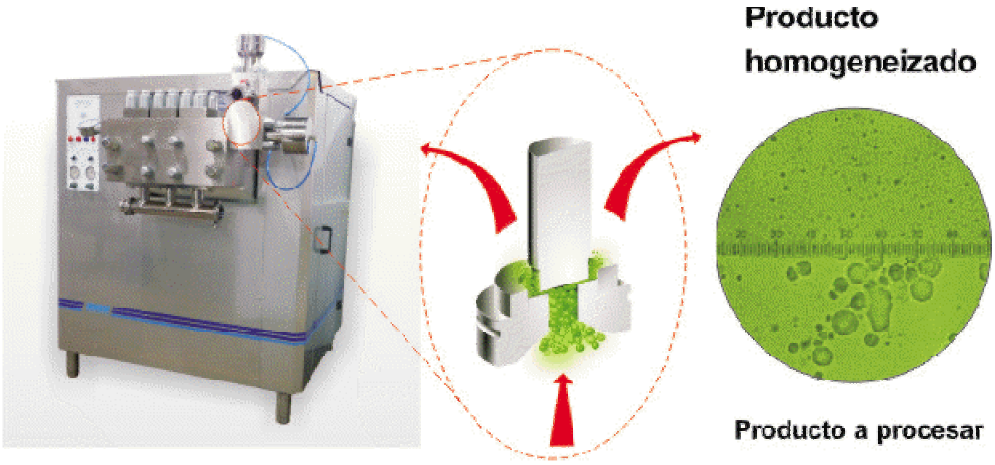

Figura 3.4. Ejemplo de un homogeneizador de alta presión comercial

A3) Ultrasonidos

Estos sistemas están formados por 3 componentes: un generador que suministra voltaje de alta frecuencia, entre 20 y 40 kHz (frecuencias más eficientes); un material piezo-eléctrico que transforma los impulsos eléctricos en mecánicos y que son transmitidos al fluido mediante un sonotrodo.

El mecanismo de cavitación crea burbujas con alternancia de presiones altas y bajas cuando explosionan, generan una gran cantidad de energía provocando la rotura de las células.

Figura 3.5. Ejemplo de la tecnología de ultrasonidos

La energía introducida en la lisis es elevada y la inactivación de los microorganismos se observa en primer lugar que la rotura celular (Chu et al. 2002).

La energía específica usualmente aplicada se encuentra en el rango de 1000 a 16.000 kJ.Kg^{-1}.ST, observándose un incremento en la producción de biogás (Salsabil et al. 2009). En sistemas *batch*, el incremento de la producción de biogás puede alcanzar rangos entre 24-40% (Bougrier et al. 2005) y rangos de 10-45% para sistema semi-continuo (Braguglia et al. 2008).

A4) Irradiación – Rayos Gamma

La radiación gamma ha sido estudiada principalmente por su efecto pasteurizador y porque consigue liberar los carbohidratos solubles de los lodos (Muller et al. 2001).

La radiación en el lodo puede ser llevada a cabo mediante una fuente de cobalto-60, que emite rayos gamma. Estos rayos penetran en el lodo y pasan a través de él, inactivando los microorganismos y descomponiendo numerosos compuestos orgánicos sin inducir en el medio ningún tipo de radioactividad residual y sin convertir el lodo en radioactivo.

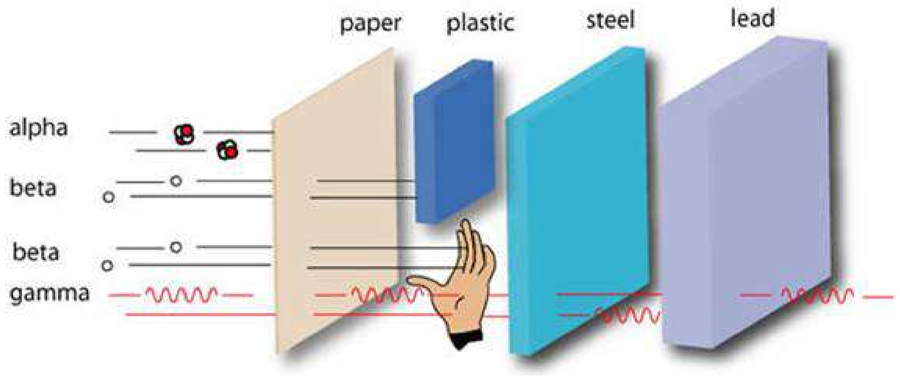

Figura 3.6. Ilustración ejemplo del pre-tratamiento de irradiación de rayos gamma

A5) Térmicos

La hidrólisis térmica destruye las paredes celulares favoreciendo el acceso al interior de las células por parte de los microorganismos.

La temperatura óptima de este proceso para lodos se encuentra entre los 150ºC o 180ºC (Anderson et al. 2002) con tiempos entre los 30 a 60 minutos.

Tratamientos a temperaturas elevadas, superior a 190ºC, origina una disminución en la biodegradabilidad debido a la formación de compuestos recalcitrantes no biodegradables.

Como ventajas adicionales resulta la disminución del tiempo de retención hidráulico (Graja et al. 2005), mejor deshidratabilidad del lodo. Como desventajas se destaca el aumento de la posibilidad de inhibición por amonio en los digestores.

Figura 3.7. Planta piloto de pre-tratamiento térmico Cambi®

B) Pre-tratamientos químicos y físico-químicos: Oxidación, tratamiento alcalino

B1) Oxidación – Pre-tratamiento con ozono

El pre-tratamiento químico más usado es el con ozono.

El objetivo del pre-tratamiento es la oxidación parcial e hidrólisis de la materia orgánica. Se evita que tenga lugar la oxidación completa, y en su lugar sucede que las moléculas de mayor tamaño rompen en otras más pequeñas. Elevadas concentraciones de ozono resultan en una aparente reducción de la solubilización de los componentes (Yeom et al. 2002).

El ozono presenta especial interés debido a que no permanece en el lodo tras su aplicación, ni da lugar a un aumento en la concentración de sales.

B2) Tratamiento alcalino

La hidrólisis alcalina es un pre-tratamiento ampliamente usado y eficaz, siendo usados los siguientes compuestos en orden de eficacia ($NaOH>KOH>Mg(OH)_2$ y $Ca(OH)_2$) (Mouneimne et al. 2003).

Durante el proceso alcalino, el pH del lodo es aumentado hasta 12, manteniéndose este valor durante un periodo de tiempo (normalmente 24 horas).

Este proceso se puede emplear para hidrolizar y descomponer lípidos, hidratos de carbono. La solubilización del lodo y su biodegradabilidad anaerobia aumentan con el aumento en la dosis y temperatura (Kim et al. 2003; Valo et al. 2004). Comparada con la hidrólisis térmica, la temperatura del tratamiento alcalino es relativamente baja, en torno a los 120-170ºC.

C) Pre-tratamientos biológicos

La desintegración bioquímica del lodo se basa en la actividad enzimática, que tiene lugar bien dentro del sistema (autolisis), o bien externamente. La lisis enzimática rompe los compuestos de la pared celular mediante una reacción catalizada por una enzima. Las reacciones tienen lugar en el rango mesófilo (55ºC) o hiper-mesófilo (entre 60-70ºC) en condiciones anaerobias y aerobias.

La tabla 3.2 recoge un resumen comparativo de los principales aspectos a destacar en las distintas opciones de pre-tratamiento.

Tabla 3.2. Procesos de pre-tratamiento de lodos de depuradora

Proceso	Ventajas	Desventajas	Resultados	Referencias
Molino de Bolas	Fiabilidad en la operación. Generación de olores nula	Erosión importante en la cámara de molienda. Problemas de atranques.	Incremento en la producción de biogás del 24%	Baier et al. 1997. Kopp et al. 1997.
Homogeneizadores de alta presión	Generación de olores nula. Facilidad de implementación en una EDAR. Mejor deshidratabilidad del lodo final.	Baja eliminación de patógenos. Problemas de atranques. Elevadas tensiones y erosión.	Incremento en la producción de biogás del 30%. Reducción del volumen del lodo de 23%.	Onyeche et al. 2007. Muller et al. 1998.
Ultrasonidos	Fiabilidad en la operación. Generación de	Erosión en el sonotrodo. Balance	Incremento en la producción	Bougrier et al. 2005. Braguglia et al.

	olores nula. Mejor deshidratabilidad del lodo. Sin problemas de atranques.	energético negativo (elevado consumo del equipo).	de biogás del 10-45%.	2008.
Rayos Gamma	Lodo obtenido libre de patógenos	Sin mejora significativa en la producción de biogás.		Muller et al. 2001.
Térmicos	Tratamiento energéticamente eficaz. Óptima desinfección del lodo. Óptima deshidratabilidad del lodo	Ensuciamiento de los cambiadores de calor. Malos olores en las corrientes gaseosas cuando no tratadas.	Incremento en la producción de biogás del 45%.	Graja et al. 2005. Valo et al. 2004.
Pre-tratamiento con ozono	Mejor deshidratabilidad del lodo.	Elevado consumo de energía.	Incremento en la producción de biogás del 16%.	Valo et al. 2004.
Tratamiento alcalino	Consumo energético bajo. Buena deshidratabilidad del lodo.	Generación de malos olores. Corrosión y ensuciamiento del equipo.	Incremento en la producción de biogás del 30-38%.	Kim et al. 2003. Valo et al. 2004.
Pre-tratamientos biológicos	Bajo consumo de energía. Sin generación de tensiones en los equipos.	Coste elevado. Importante generación de olores.	Incremento en la producción de metano del 26%.	Gavala et al. 2003.

3.4.2. Alternativas de pre-tratamiento de biomasa lignocelulósica

La tabla 3.3 recoge un resumen de algunos pre-tratamientos referenciados en bibliografía.

La investigación de pre-tratamientos a biomasa lignocelulósica se ha realizado fundamentalmente en materia de biocombustibles, si bien el creciente interés por la digestión anaerobia ha conducido al aumento de la investigación de estos pre-tratamientos como etapa previa a la digestión anaerobia de este tipo de residuos.

Tabla 3.3. Procesos de pre-tratamiento de biomasa lignocelulósica

Proceso	Tipo	Observaciones	Referencias
Molienda	Molino de Bolas	Reducción del tamaño de partícula. Sin eliminación de la lignina. Elevado consumo de energía.	Da Silva el al. 2010. Mais et al. 2002.
Irradiación	Microondas Rayos-Gamma Ultrasonidos	Posible degradación de la celulosa sin eliminación de la lignina. Elevado coste de operación.	Sapci et al. 2013. Jackowiak et al. 2011. Pérez-Elvira et al. 2010 a. Pérez-Elvira et al. 2009. Sólyom et al. 2011.
Térmicos	Cocimiento Explosión de vapor	Parcial o completa hidrólisis de la hemicelulosa cuando operación a elevadas temperaturas. Sin adición de productos químicos. Posible recuperación energética del vapor.	Ferreira et al. 2013. Pérez-Elvira et al. 2010 b. Horn et al 2011. Vivekanand et al. 2012. Han et al. 2010.
Tratamiento Ácido	Ácido sulfúrico, clorhídrico o fosfórico	Aumento del área de superficie de tratamiento. Parcial desintegración de la lignina. Parcial o completa	Yang and Wyman, 2008. Ping et al. 2011.
Tratamiento Alcalino	Hidróxido de sodio, potasio, calcio o		Chandra et al. 2012 b.

	magnesio	hidrólisis de la hemicelulosa	Kim et al. 2006.
Agentes Oxidantes	Oxidación húmeda		Kuman et al. 2009. Schmidt and Thomsen, 1998.
Biológicos - Hongos		Hidrólisis parcial de la hemicelulosa. Bajos costes energéticos. Tiempos de desarrollo muy largos.	Kurakake et al. 2007.

3.5. Definición de la alternativa de trabajo en la presente tesis

3.5.1. Comparación de alternativas

El amplio espectro de opciones posibles presentadas en el apartado anterior ha sido evaluado comparativamente atendiendo a una serie de aspectos, descritos a continuación, con el objetivo de seleccionar la tecnología de pre-tratamiento a emplear en la presente tesis:

- Aumento en la solubilización: liberalización del material celular como consecuencia de la rotura de las paredes celulares en el tratamiento, permitiendo que una mayor cantidad de residuo sea susceptible de degradación anaerobia.
- Aumento de la producción de biogás: con el aumento de la solubilización del residuo, la cantidad de materia orgánica disponible para los microorganismos anaerobios es mayor, y por lo tanto, favorecerá la producción de biogás.
- Reducción del volumen final: un mayor rendimiento en el proceso anaerobio, llevará a una reducción en la cantidad de residuo no degradado.

- Esterilización y posibilidad de uso agrario del residuo: De forma a cumplir con los límites de viabilidad de los residuos que impone la legislación (1999/31/CE) para que puedan ser aplicados al terreno, es importante que el tratamiento favorezca una adecuada desinfección del residuo.
- Coste de inmovilizado y operación: Se trata de un factor clave para determinar la posibilidad de implantación de la tecnología seleccionada.

3.5.2. Selección y justificación de la alternativa de trabajo

La comparación entre las distintas alternativas ha conducido a la elección de la **tecnología de hidrólisis térmica de residuos sólidos** como alternativa a desarrollar en el presente trabajo.

Por otro lado, es obligado señalar que el proyecto que ha permitido el desarrollo de esta tesis (“Thermal Hydrolysis Process as a Pretreatment to Anaerobic Digestion of Solid Wastes”) ha sido financiado por la empresa Cambi®, líder mundial en procesos de hidrólisis térmica, y por tanto interesada en el presente estudio.

Una serie de argumentos apoyan la elección de este tratamiento y se recogen a continuación:

a) Se trata de un proceso de fácil instalación en las depuradoras ya existentes, sin necesidad de llevar a cabo modificaciones en el proceso convencional. Solamente es necesaria la introducción de dispositivos adicionales y equipos necesarios para la hidrólisis térmica, pero no se necesita alterar la configuración inicial.

b) La eficacia de este proceso es muy elevada, dado que el tratamiento de hidrólisis térmica produce un aumento en el nivel de materia orgánica disuelta en un factor de 5 a 20 (dependiendo del tipo de residuo). Este aumento se traduce en un incremento en la biodegradabilidad del residuo, que a su vez se refleja en una mayor cantidad de biogás producida en el proceso de digestión anaerobia que sigue al tratamiento térmico.

c) La hidrólisis térmica destaca frente a otras opciones porque permite recuperar parte de la energía empleada (a través del incremento del metano producido), mientras que en otros procesos no es posible. A pesar de que el consumo de energía que supone es elevado, la recuperación de energía hace que el proceso sea ventajoso frente a otras alternativas que consumen menos energía pero cuyo balance global resulta más desfavorable.
d) Esta recuperación de energética por obtención de biogás justifica la viabilidad del proceso desde los puntos de vista medioambiental y económico. Dado que no sólo se elimina el problema, sino que además se valoriza energéticamente el residuo, el proceso resultante tiene mucho que decir en materia de sostenibilidad.
e) Se trata de una tecnología ya desarrollada a escala real, y por tanto su viabilidad técnica está garantizada.
f) Esta alternativa permite el uso agrícola del residuo resultante, puesto que el tratamiento térmico asegura unas condiciones de pasteurización adecuadas, al alcanzarse temperaturas elevadas durante un tiempo suficiente. En este sentido, la eliminación de patógenos es total, situación que no se da en otras alternativas.

Por los argumentos anteriores se puede afirmar que se trata de una **alternativa viable técnica y económicamente,** sin necesidad de ser completada con otra técnica.

Finalmente, de entre las distintas opciones de realizar el tratamiento térmico (calentamiento directo con vapor, calentamiento indirecto, microondas, cocimiento, explosión de vapor), se selecciona la alternativa de pre-tratamiento térmico por inyección directa de vapor y posterior explosión de vapor (“*steam explosión*”) basado en la experiencia del grupo de investigación en pre-tratamiento térmico de lodos de depuradora.

3.5.3. Hidrólisis térmica – revisión de tecnologías comerciales

Actualmente existen en el mercado ocho procesos de pre-tratamiento térmico de bioresíduos, cada uno de ellos con un esquema específico, pero con similares condiciones de operación.

El artículo que sigue, correspondiente a una comunicación presentada en el Congreso *“13Th World Congress on Anaerobic Digestion – Recovering (bio) Resources for our World. IWA – International Water Association. June 25-28, 2013. Santiago de Compostela, Spain”*, recoge una revision y comparative de las distintas tecnologías de pre-tratamiento técnico de residuos existentes.

Thermal hydrolysis pre-treatment of biosolids: A review on commercial processes

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Abstract
Several commercial pre-treatment processes prior to anaerobic digestion have been developed in response to tightening regulations and decrease in disposal options. The first processes (Cambi® and Biothelys®) aimed to enhance biodegradability and sanitization of municipal sludge in a batch process. Subsequent continuous process have been developed (Exelys®, Lysotherm®, Turbotec®) and the treatment has been extended to other biosolids such as agriculture wastes, OFMSW or animal by-products (TPH®, TPP®, BioRefinex). Although similar operation conditions and benefits are offered (biodegradability increase, sludge reduction, sanitization, dewaterability), scarce references to real performance are available for most of them, except for Cambi and Biothelys.

Keywords: Anaerobic digestion; biosolids; commercial; thermal hydrolysis; review

Introduction

In response to the current bottleneck for biosolids disposal, the possibilities to optimize the anaerobic digestion process (biodegradability and degradation rate increase, higher digesters load, sludge reduction) together with achieving some other benefits (sanitization, dewatering) are a subject of major concern. The pre-treatment of waste activated sludge before anaerobic digestion is generally proposed as the most efficient and sustainable alternative (Carrère et al, 2010).

Among all the existing pre-treatment alternatives (thermal, chemical, mechanical, electrical, ultrasound) thermal hydrolysis is a promising technology. Technical and especially economical constraints of most of the technologies have limited their scale-up and lab-to-field implementation.

There are several commercial thermal pre-treatment processes nowadays, for different applications and with different operation schemes. The first processes were developed for the treatment of sludge, but the technology has been extended to the treatment of other biosolids (food waste, agriculture biosolids, animal by-products) and new processes have been developed with different objectives (digestion improvement, sanitization, biosolids quality). The technologies differ in many aspects, such as: operation (batch or continuous), reactor configuration, operation conditions (pressure, temperature, time), energy integration scheme (key for the process economics).

This study consists of a literature review performed from the information available in journal articles, conference proceedings, reports and web-sites, with the purpose of summarizing and comparing the different commercial existing thermal hydrolysis pre-treatments for biosolids.

Thermal pretreatment commercial processes

Cambi®.

Developed by the Norwegian company Cambi, in 1995. The process is a high-pressure steam pre-treatment for anaerobic digestion of sludge and bio-waste (Cambi).

The technology consists of a series of reactors including a pulper vessel, a hydrolysis reactor and a flash tank. The system operates batchwise. Solids are first dewatered (10-16% dry solids), and then transferred to the pulping vessel where it is pre-heated to 80-97ºC with recycled steam from the flashing of other parallel reactor. The preheated sludge is then sent to the thermal hydrolysis reactor that operates at a temperature of 160-180ºC (6-9 bar) for about 20-30 minutes with direct steam injection. After the thermal treatment, the sludge is transferred to the flash tank operating at atmospheric pressure. The hydrolyzed sludge is then cooled for mesophilic anaerobic digestion.

The process is nowadays operating in more than 20 plants (Panter and Kleiven, 2005; Kepp et al, 2000; Steve and Panter, 2002).

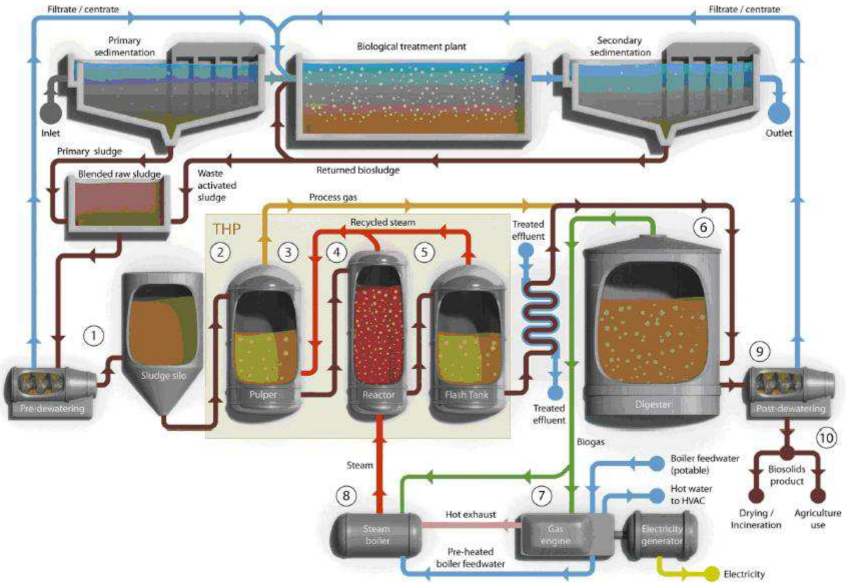


Figure 3.8. – Cambi® process

Biothelys®.

Developed by the French Company Veolia (Veolia Water, 2012a) for treating sludge prior to anaerobic digestion. The process is similar to the Cambi process, with the exception that the Biothelys system has no pulper or flash tank, just reactors of the same size operating in parallel.

The process consists of 2-3 hydrolysis reactors working in parallel out of phase with each other, going through a 150-170 minutes multi-step cycle. Dewatered sludge (15% DS) is preheated in the reactor with recycled flash steam from the other reactor. Heating to the hydrolysis temperature (150-170ºC; 7-9 bar) is completed by injecting live steam, and after the desired retention time (30-60 min) the pressure is reduced by flash. The hydrolysed sludge is stored and cooled, and fed to digestion (Chauzy et al., 2007).

The process was first operated in 2006 and nowadays operates in 4 plants (Veolia Water, 2012a).

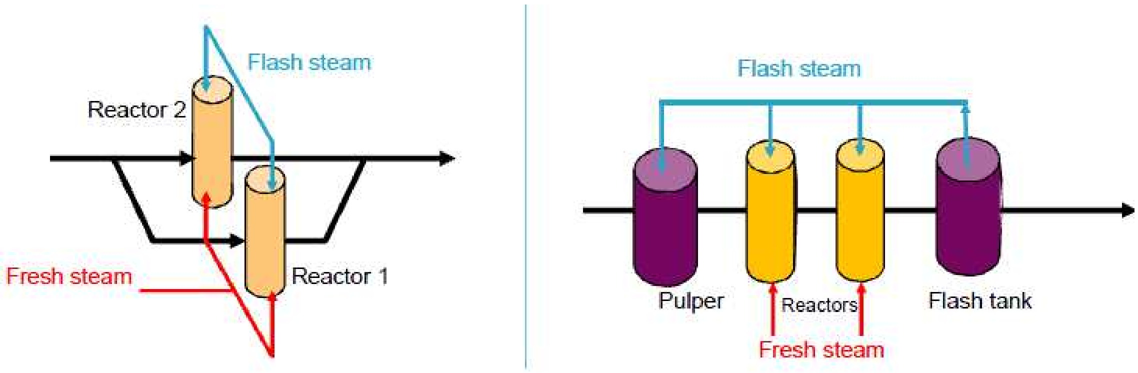


Figure 3.9. – Comparison between industrial process by Veolia (left) and Cambi® (right)

Exelys®.

Similar treatment to Biothelys, sold by Kruger, a subsidiary of Veolia Water (Veolia Water, 2012b). This process was developed as a continuous process that handles biosolids with a dry solids content greater than 20% with the objective of reducing the operation cost compared to the batch system.

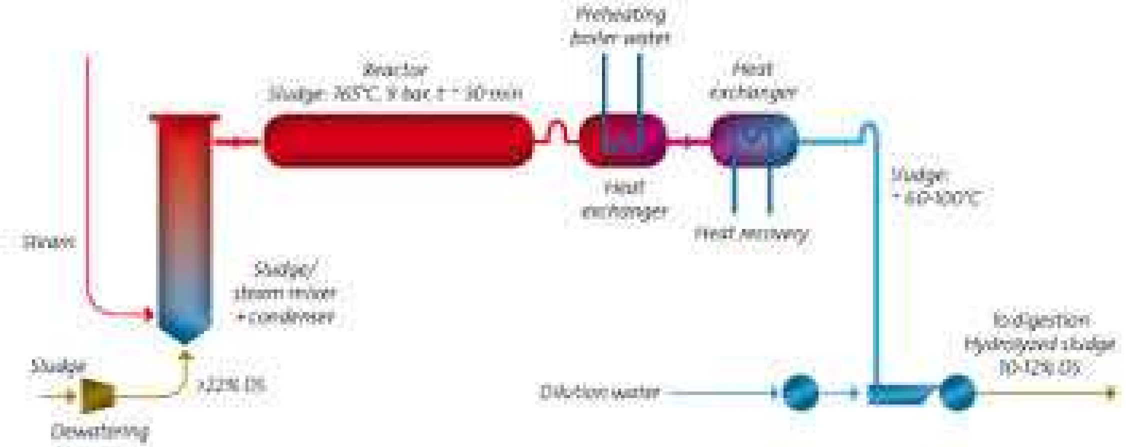


Figure 3.10. – Exelys system, sold by Kruger

Dewatered solids and steam are continuously fed to the steam condenser section, where the steam condenses transferring heat to the biosolids raising the temperature to the desired value. Then the biosolids enter the reactor and flow at low velocity resulting in plug flow, and finally they go to a heat exchanger system where they cool before entering the digestion (Gurief et al., 2011).

The first Exelys plant began to operate in 2010, with the configuration Digestion-Lysis-Digestion (Krüger, 2011).

TPH® (thermal-pressure-hydrolysis).

Trademarked process from the ATZ development center. R. Scheuchl and Thöni appear as licensees (R. Scheuchl GmbH; Thöni, 2010).

This process can be used to treat a great variety organic materials (sewage sludge, food and kitchen waste, animal by-products, slaughterhouse waste), limited to grinding to particle size <50 mm. The wastes are hydrolyzed and sanitized at high pressure and high temperature (Prechtl, 2006). The operation is continuous, involving storage tank, high pressure pump, controlled pressure release valve and heat exchanger pipes. The system operation is a two step heating procedure: first by direct steam injection and secondly indirect in a coaxial heat exchanger run with thermo-oil (220 °C at 25 bar for 20 min). The heated material is then mixed with water and anaerobically fermented in a biogas reactor. The biogas is used in the co-generation plant. The energy necessary for the thermal pre-treatment is drawn from the radiant heat of the CHP.

Scarce references have been found about full scale plants (Actclean, 2011), and no information about real performance is available.

Figure 3.11. – Thermal-pressure-hydrolysis process

Thermo-pressure preparation (TPP).

Also protected by a patent and utility model, uses high pressure and temperature followed by expansion to hydrolyze any biomass. It is proposed to be used with lignocellulosic biomass as a pre-treatment to get bioetanol (fermentation) or biogas (digestion), or with proteinaceous biomass of plant and animal origins to form soluble products useful in cosmetics.

The process operates in continuous: Raw material is first milled and grinded to create a pumpable suspension, fed to the reactor together with steam. Shock expansion occurs after the passage, and the waste vapour produced can be used to preheat the feeding. No information is given about operation conditions. The process uses waste gas heat from electrical energy production to produce the thermal energy for the hydrolysis.

The process is commercialized by the Czech company NWT (NWT, 1992), but no reference to full-scale operation and performance is available.

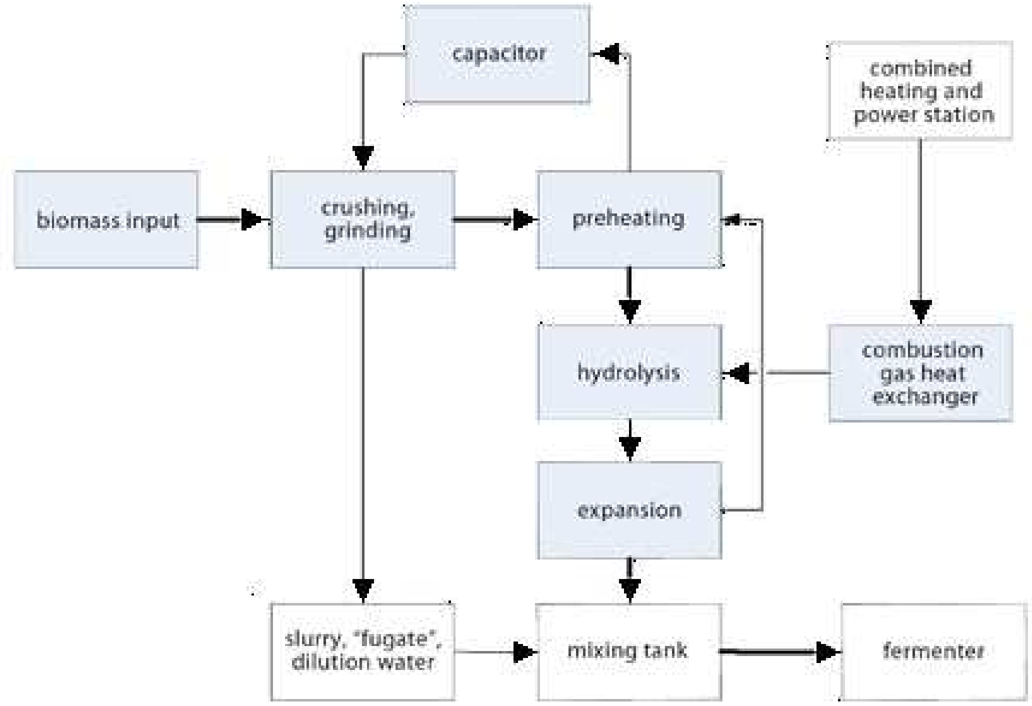


Figure 3.12. – Thermo-pressure preparation process

Lysotherm®.

Patented system for the thermal hydrolysis of low viscous to medium-viscous organic sludge (dry solids 6-8%), in particular sewage sludge from WWTP.

The operation is based in an indirect multi-stage thermal system. In a first stage (regenerative circuit) the sludge is preheated and then heated to the hydrolysis temperature (175ºC, 30-60 min) in a tubular reactor (thermal oil circuit). The regenerative circuit uses water as the transfer medium, recovering the heat from the hydrolysed sludge to preheat the sludge. The thermal oil in the process heat circuit is heated by the CHP exhaust gas heat.

The Stulz H+E group commercializes the technology (SH+E group, 2012). No references to full-scale plants are given, except for a plant in Lingenmill that is expected to be finished in 2012.

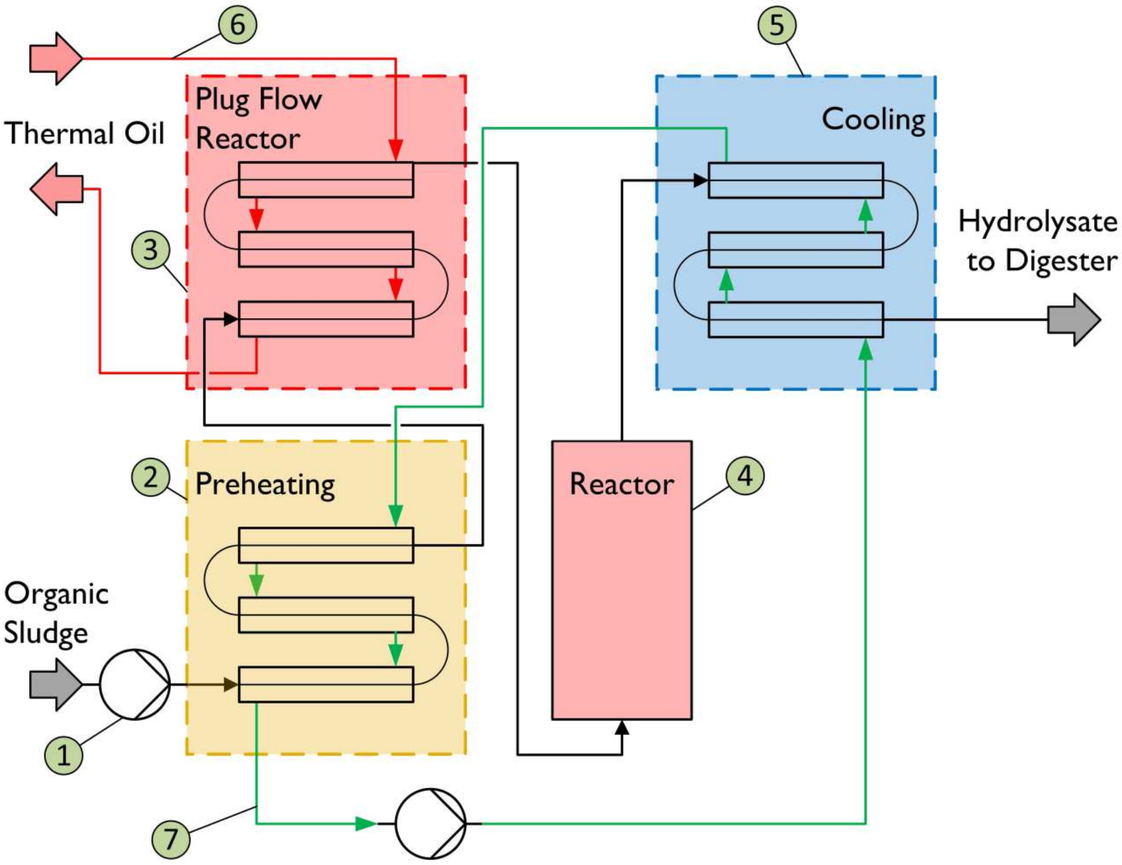


Figure 3.13. – Lysotherm process

BioRefinex.

Patented technology (Biorefinex, 2012), developed by Biosphere Technologies, utilizes thermal hydrolysis to process animal by-products and carcass material using a combination of high temperature and high pressure to break down complex proteins and inactivate prions. The operation conditions are not indicated in the process description, but references to 180ºC, 12 bar and 2 hours have been found (Gibson L, 2011).

The first full demonstration facility (Lacombe Biorefinery) will start in 2013. Therefore, there are no results from real operation.

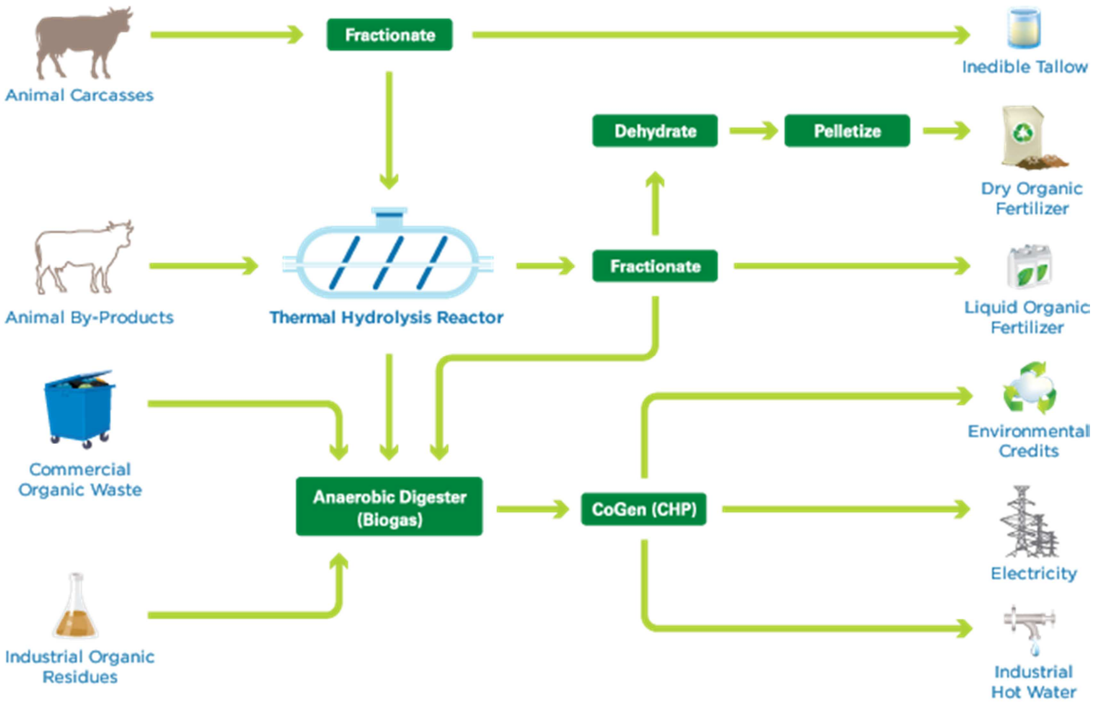


Figure 3.14. – Biorefinex process

Turbotec®.

Hydrolysis organic material in a reactor at high temperature and pressure, prior to anaerobic digestion. After thickening, sludge is fed to the hydrolysis reactor, heated with waste heat from the gas engine (GMB, 2011).

The commercializing company (Sustec, 2011) offers three different applications: Turbotec I®, a continuous process for sewage sludge; Turbotec II®, a batch process for greenwaste and straw; and Turbotec Industrial ®, for processing industrial sludge.

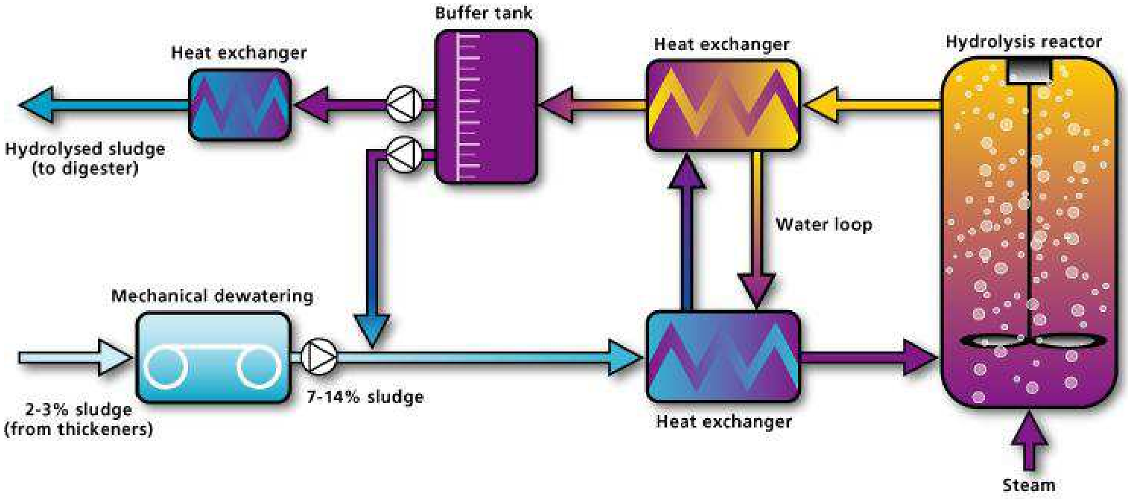


Figure 3.15. – Turbotec process

Comparison of treatment methods

In order to roughly compare the existing processes, the available information is summarized in Table 3.3. Although there are many knowledge gaps, some interesting aspects can be commented.

Table 3.3. Comparison of operation and performance reported for the commercial thermal pre-treatment processes

		Cambi	Biothelys	Exelys	TPH	TPP	Lysotherm	BioRefinex	Turbotec
References to plants		20	4	1	2	1	1	1	1 (pilot)
Operation type		Batch	Batch	Cont.	Cont.	Cont.	Cont.	N.A.	Batch/Cont.
%TS in feeding		12-16	10-15	>20		N.A.	6-8	N.A.	10
Operation conditions	T (ºC)	160-180	150-170	N.A.	180-230	N.A.	175	160	150
	P (bar)	6-9	7-9	N.A.	20-30	N.A.	5-15	12	5
	t (min)	20-30	30-60	N.A.	20-60	N.A.	30-60	120	N.A.
% biogas increase*		100-150	50	20-40	+	30	20-50	+	30-50
% VS removal		60-70	45-50		+	N.A.	N.A.	N.A.	N.A.
Pasteurization		+	+	+	+	N.A.	N.A.	+	N.A.
%DS in dewatered cake		30-40	35	N.A.	+	+	32	N.A.	>30
Viscosity reduction		+	+	+	N.A.	N.A.	N.A.	+	N.A.

* respect conventional

N.A.: not available

A first key point to compare is the application field and objective of the different processes. Most of the processes focus to enhance the biodegradability of the biosolids to be treated: Cambi®, Biothelys®, Exelys®, Lysotherm® and Turbotec I® for sludge (Cambi® also processes OFMSW), the TPP® process and Turbotec II® for lignocellulosic biomass, and the TPH®-method for any type of waste. A second objective of the thermal hydrolysis is the sanitization (main objective of the Biorefinex process, but also mentioned by Cambi®, Biothelys®, Exelys® and TPH®).

Regarding the operation conditions, the technologies have three aspects in common:

1) the operation with concentrated biosolids,
2) no use of chemicals, and
3) operation conditions in the range of 150-230ºC for 20-60 minutes.

However, the process configuration, heating mechanism and energy recovery scheme varies in all the technologies. While the origin of the thermal pre-treatment was a batch process (Cambi® and Biothelys®), the more recent developments claim continuous operation, searching for more cost-effective operation by exploiting the energy recovery. However, detailed costs estimate (capital and operation and maintenance) are not available.

Regarding the process performance, globally most of the processes offer the same qualitative benefits. However, only Cambi® and Biothelys® give references to support the advantages offered.

Finally, scarce references to disadvantages have been found. Some issues reported by Cambi® are: system complexity, need for high level operator training, shutdowns (regulatory inspections and approved maintenance), and increase in soluble inert fraction and ammonia in the recycled stream. While not mentioned, all the technologies may also be subjected to these and even more concerns.

Conclusions

Eight different thermal hydrolysis technologies are nowadays commercialized for the treatment of biosolids (five for sludge, one for lignocellulosic biomass, one for animal by-products and one for any type of waste). Although there are many gaps in the information available, it can be stated that the operation conditions and performance are globally comparable, although the operation schemes (batch/continuous, reactor configuration and energy integration) differ among them. Only Cambi and Veolia report information supported with real data from full-scale installations.

Capítulo 4

Objetivos

El objetivo global definido en el capítulo 2 “OPTIMIZACIÓN DE LA DIGESTIÓN ANAEROBIA DE DISTINTOS RESÍDUOS ORGÁNICOS” queda concretado tras la investigación realizada en el capítulo 3 en dos aspectos:

1 - Definición de los residuos específicos a tratar.

2 – Tecnología de optimización: pre-tratamiento de hidrólisis térmica.

Por tanto, el **objetivo concreto** de la presente tesis se define como “ **OPTIMIZACIÓN DE LA DIGESTIÓN ANAEROBIA DE DISTINTOS RESIDUOS ORGÁNICOS INDUSTRIALES, AGRÍCOLAS, GANADEROS Y URBANOS MEDIANTE LA INTRODUCCIÓN DE UN PRE-TRATAMIENTO DE HIDRÓLISIS TÉRMICA CON EXPLOSIÓN DE VAPOR”.**

Como se definirá en el capítulo 5 correspondiente a “Materiales y Métodos” el estudio de optimización se ha realizado con las siguientes pautas:

- Mediante la realización de ensayos de potencial metanogénico (*Biochemical Methane Potential – BMP*).
- Pre-tratamiento de hidrólisis térmica a distintas condiciones de operación (temperatura, tiempo).
- Tratamiento matemático de los resultados.

Habiendo definido cinco residuos concretos a estudiar, el desarrollo de la tesis se concreta en **cinco objetivos específicos**:

1) Hidrólisis térmica como pre-tratamiento previo a digestión anaerobia de **bagazo de cerveza** (apartado 6.1).
2) Hidrólisis térmica como pre-tratamiento previo a digestión anaerobia de **cáscara de naranja** (apartado 6.2).
3) Hidrólisis térmica como pre-tratamiento previo a digestión anaerobia de **paja de trigo** (apartado 6.3).

   a) Optimización de condiciones de operación – “*Influence of thermal pretreatment on the biochemical methane potential of wheat straw”.*

   b) Estudio de otros parámetros de operación – “*Biomethane potential of wheat straw: Influence of particle size, water impregnation and thermal hydrolysis”.*
4) Hidrólisis térmica como pre-tratamiento previo a digestión anaerobia de **purines de cerdo –** “*Thermal hydrolysis pretreatment to enhance biodegradability of the separated solid fraction of pig slurry*” (apartado 6.4).
5) Hidrólisis térmica como pre-tratamiento previo a digestión anaerobia de **lodo de EDAR –** *“Thermal pretreatment and hydraulic retention time in continuous digesters fed with sewage sludge: Assessment using the ADM1”* (apartado 6.5).

Cada uno de dichos objetivos corresponde a un apartado concreto dentro del capítulo 6 de “Resultados y Discusión”. En concreto, para los residuos paja de trigo, purines de cerdo y lodos de depuradora, los estudios realizados corresponden a los 4 artículos que se referencian en los correspondientes apartados.

Capítulo 5

Materiales y Métodos

5.1. Hidrólisis Térmica - Plantas piloto

5.1.1. Planta piloto de Cambi®

a) Residuos con que se ha empleado: paja, cáscara de naranja y bagazo de cervecera

b) Descripción de la planta piloto: Se trata de una planta piloto de hidrólisis térmica perteneciente a la empresa Cambi® y ubicada en la estación depuradora de aguas residuales de Salamanca.

La planta cuyo esquema se muestra en la figura 5.1, consiste en un reactor de 30 litros de capacidad y un tanque flash con un depósito para recolectar la biomasa pre-tratada. El calentamiento de la biomasa en el reactor se realiza mediante inyección directa de vapor generado en una caldera de 25 kW de potencia con una capacidad máxima de generación de vapor de 34 bar (240ºC).

c) Procedimiento de operación

El modo de operación es por cargas (*batch*), combinándose el efecto de cocimiento y explosión de vapor.

La biomasa es alimentada al reactor por la parte superior (tolva) usando la válvula motorizada (V1). El vapor se introduce al reactor por la base (V2-V3) calentando el residuo durante el periodo de tiempo establecido.

Los parámetros de control corresponden a las condiciones de operación deseadas: presión (temperatura correspondiente al equilibrio líquido-vapor) y tiempo. El control de la presión se realiza automáticamente mediante un lazo que actúa automáticamente sobre la válvula V2.

Transcurrido el tiempo de operación deseado, la válvula V4 abre automáticamente y súbitamente y la presión del reactor disminuye de inmediato hasta la presión atmosférica liberándose la biomasa pre-tratada al tanque de *flash* mediante un efecto de "*steam explosion*".

El residuo hidrolizado es colectado posteriormente en el depósito de recogida.

El vapor liberado que no ha condensado en el tanque *flash* es conducido a un filtro de carbón activado donde se eliminan los olores.

Antes del inicio de cada experimento, el reactor es precalentado durante aproximadamente 5 minutos a la misma temperatura seleccionada para el pre-tratamiento, de forma que se minimice la condensación (y por tanto la dilución de las muestras).

Las figuras 5.1 y 5.2 presentan el esquema e imágenes de la planta piloto Cambi®

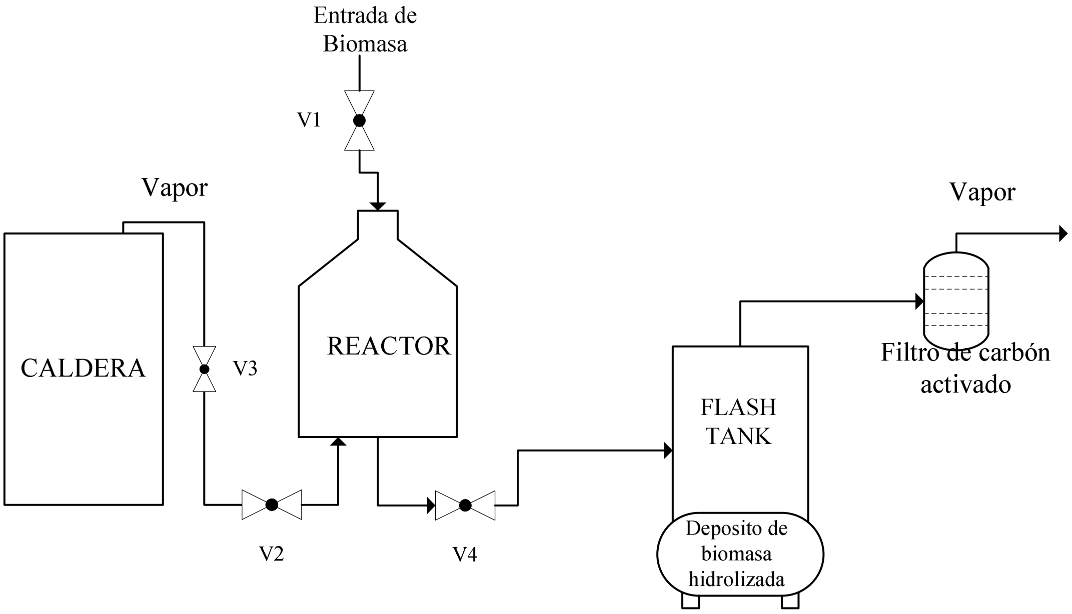


Figura 5.1 – Esquema planta de hidrólisis térmica Cambi®. (V- válvula)

(a) (b)

Figura 5.2 – Planta de hidrólisis térmica Cambi®: (a) Tolva de alimentación y reactor; (b) Tanque flash y depósito de recogida de la biomasa tratada.

5.1.2. Planta piloto de la Universidad de Valladolid

a) Residuos a que se ha empleado: purines y lodos de depuradora.

b) Descripción de la planta: Se trata de una planta piloto diseñada y construida en el marco de un proyecto de hidrólisis térmica de lodos de EDAR, y ubicada en el departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Universidad de Valladolid. Por ello, su aplicación a residuos sólidos es limitada, si bien resulta viable y muy fiable para pastas viscosas.

La planta cuyo esquema se muestra en la figura 5.3, consiste en un reactor de 2 litros de capacidad (1L de volumen útil), calentado con vapor procedente de una caldera (capacidad máxima: 10 bar), y un tanque de *flash* para recoger el residuo tras la descompresión

c) <u>Procedimiento de operación</u>

Al igual que la unidad Cambi® descrita previamente, la operación es por cargas, si bien en este caso el control de la operación se realiza de modo manual, actuando sobre las válvulas V1 y V2 como se describe a continuación. Al igual que la unidad Cambi®, el tratamiento en esta planta combina cocimiento y efecto de “*steam explosion*”.

Antes de empezar la operación, la planta piloto se precalienta mediante inyección de vapor para minimizar la condensación durante la operación posterior. El residuo a tratar se introduce en el reactor de hidrólisis donde se mantiene a la presión y temperatura de operación deseados, controlando la temperatura mediante apertura de la válvula manual V1 que permite el paso de vapor procedente de una caldera. Trascurrido el tiempo de operación deseado, se descomprime el reactor abriendo manualmente de modo súbito la válvula V2, y recogiéndose el residuo en el tanque de *flash*.

Las figuras 5.3 y 5.4 muestran esquema e imagen de la planta piloto

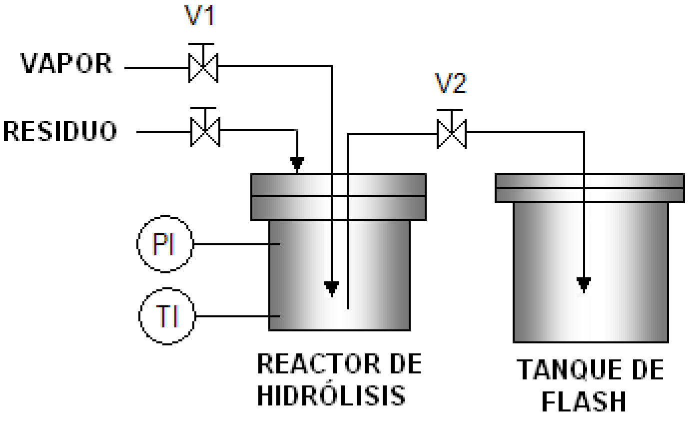


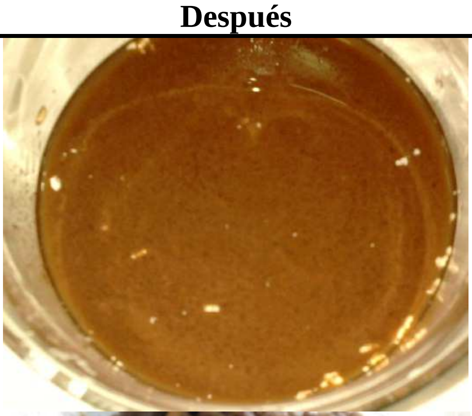
Figura 5.3. Esquema planta piloto de hidrólisis térmica de la Universidad de Valladolid

Figura 5.4. Planta piloto de hidrólisis térmica de la Universidad de Valladolid

5.1.3. Imágenes pre y pos-tratamiento

La tabla 5.1 muestra una serie de imágenes de distintos residuos antes y después del pre-tratamiento, poniendo de manifestó el cambio radical en aspecto visual que sufre la biomasa tras el tratamiento.

Tabla 5.1. Imágenes de algunas biomasas antes y después de la hidrólisis térmica

	Pre-tratamiento		
Residuo	**Antes**	**Después**	**Condición**
Cáscara de naranja			170ºC, 30 min
Paja			220ºC, 1 min
Lodo de depuradora			170ºC, 40 min

5.2. Digestión anaerobia - Biodegradabilidad

5.2.1. Ensayos de biodegradabilidad

El fundamento de base de los ensayos de biodegradabilidad consiste en simular la digestión anaerobia en un ensayo controlado, introduciendo un sustrato orgánico en el cultivo anaerobio y realizando un seguimiento de la generación de biogás y metano.

Los ensayos de biodegradabilidad anaerobia permiten determinar una serie de características del residuo, como son:

- Fracción biodegradable de un residuo o corriente en condiciones anaerobias. Las sustancia presentes en un agua residual o residuo sólido tienen unos porcentajes de biodegradabilidad muy variados, desde totalmente biodegradables a recalcitrantes.

- Potencial metanogénico del residuo (*Biochemical Methane Potential - BMP*). Corresponde a la cantidad de metano generada en la descomposición anaerobia por unidad de residuo.

- Viabilidad del tratamiento de un residuo. El número de sustancias que se tratan mediante la tecnología anaerobia va aumentando progresivamente, por lo que resulta necesario el conocimiento de la respuesta del sistema ante la entrada de una nueva corriente o compuesto.

- Variación que sufre la biodegradabilidad de un residuo ante un pre-tratamiento. Como se ha descrito, son cada vez más las tecnologías que se están desarrollando con el objetivo de incrementar la biodegradabilidad de los residuos orgánicos. Los ensayos de biodegradabilidad permiten evaluar la influencia que un pre-tratamiento de lisis tiene en el proceso de digestión anaerobia, comparando las cantidades de metano producidas por el residuo tanto fresco como el sometido al proceso de tratamiento de hidrólisis.

En la presente tesis, los ensayos de biodegradabilidad son la metodología clave para determinar la influencia de la hidrólisis térmica en el potencial metanogénico de distintos residuos en distintas condiciones de operación. Dada la gran cantidad de situaciones ensayadas, la operación de digestores anaerobios es claramente inviable.

5.2.2. Biodegradabilidad anaerobia

La biodegradabilidad es la propiedad intrínseca de una sustancia que hace referencia a la tendencia que ésta tiene en ser biológicamente degradada. Se define como sustancia biodegradable aquella que puede ser descompuesta mediante la acción de los microorganismos. En función del grado de transformación es posible distinguir dos tipos de biodegradabilidad:

- Biodegradabilidad primaria o hidrolítica/acidogénica: Es la transformación de la sustancia a nivel estructural, donde pierde alguna de su propiedad específica y forma nuevos compuestos que podrán ser biodegradables. Algunos compuestos no son capaces de completar la ruta de degradación durante el proceso de biodegradación anaerobia, como es el caso por ejemplo de los ácidos grasos volátiles.
- Biodegradabilidad final o metanogénica: Es la transformación completa de la sustancia en compuestos inorgánicos y algunos productos no biodegradables resultantes del proceso metabólico celular. En la biodegradabilidad metanogénica se obtienen como principales productos finales el metano y el dióxido de carbono, bien como otros compuestos inorgánicos (H_2, NH_3, N_2, NO_x, H_2S).

La biodegradabilidad se suele expresar como el porcentaje de sustancia que es degradado en un periodo de tiempo dado en comparación con la cantidad teórica que podría ser convertida estequiométricamente, en base a su análisis elemental.

5.2.3. Potencial metanogénico o de biogás

El potencial metanogénico de un residuo (Biochemical *Methane Potential* - BMP) se define como la producción específica ultima de metano para un tiempo de degradación infinito. En la práctica el ensayo tiene una duración finita y el potencial se obtiene por extrapolación de la curva. Si en lugar de cuantificar la cantidad de metano se determina la cantidad de biogás total tendremos el potencial de producción de biogás. Debido a la mayor influencia de las condiciones ambientales en la solubilidad del dióxido de carbono, y por consiguiente en la composición del biogás, el potencial metanogénico es un parámetro más representativo y fiable que el potencial de producción de biogás.

El BMP se suele expresar como el volumen de metano producido en condiciones normales (0ºC, 1atm) por unidad de residuo alimentado (kg SV o kg DQO). Debido a la complejidad de los residuos, no es posible conocer normalmente su composición, por lo que se utiliza la demanda química de oxigeno (DQO) o los sólidos volátiles (SV) para describir su concentración. Conocida la composición del residuo es posible determinar la relación DQO/SV a partir de la oxidación:

$$C_aH_bO_c + (a - b/4 - c/2).H_2O \rightarrow (a/2 - b/8 + c/4).CO_2 + (a/2 + b/8 + c/4).CH_4$$

Donde para un compuesto $C_nH_aO_b$ se tiene que

$$DQO/_{SV} = \frac{\left(n + \frac{a}{4} - \frac{b}{2}\right) * 32}{12n + a + 16b} \qquad (5.1)$$

El potencial metanogénico <u>teórico</u> de un compuesto $C_nH_aO_b$ se puede determinar a partir de la ecuación de Buswell:

$$B_{o,th} = \frac{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right) * 22.4}{12n + a + 16b} = STP\ L\ CH_4/g\,.SV \qquad (5.2)$$

Este valor es un límite superior ya que debido a los siguientes factores no se puede alcanzar (Angelidaki y Sanders, 2004):

- Parte del sustrato se utiliza en la síntesis de biomasa (5-10%).
- A un tiempo finito de ensayo parte de la materia orgánica se pierde con el efluente (10% aprox.).
- Existen compuestos orgánicos que no son biodegradables en condiciones anaerobias.
- Partes de la materia orgánica son inaccesibles para los microorganismos. Fenómenos de adsorción.
- Pueden existir limitaciones de nutrientes o elementos traza que impidan la degradación.
- La presencia de compuestos inhibitorios lleva a resultados de potenciales inferiores a los que se obtendrían en condiciones óptimas.
- En aguas con nitratos y sulfatos los microorganismos desnitrificantes y sulfatoreductores están favorecidos frente a los metanógenos. La cantidad de materia orgánica disponible para la metanogénesis será inferior y por lo tanto, la cantidad metano producido disminuirá.

En la práctica, el potencial metanogénico se determina mediante un ensayo controlado.
En el apartado que sigue se describe los diferentes factores y condiciones de operación que influyen en el desarrollo y resultados de los BMP, seleccionándose el modo de trabajo en los BMP realizados en la presente tesis.

5.2.4. Condiciones seleccionadas para los ensayos BMP

El resultado de potencial metanogénico (BMP) obtenido en el ensayo de biodegradabilidad se ve influido por condiciones físicas, químicas y fisiológicas. La mayoría de las metodologías existentes para la determinación de biodegradabilidad operan en discontinuo, a diferencia de la operación a escala real, que transcurre en continuo. De esta forma, los resultados de un BMP no son directamente extrapolables a escala real, si bien permiten obtener una referencia del potencial biodegradable de la sustancia, y lo que es más importante: comparar distintos residuos o la influencia de determinados tratamientos sobre la biodegradabilidad de los residuos (objetivo de la presente tesis).

A continuación se describen los principales parámetros que influyen en los ensayos de BMP, y el valor o rango de trabajo seleccionado para cada uno de ellos.

a) Temperatura

Como ha sido descrito en el capítulo 3 (apartado 3.3.2), la cinética del proceso de degradación anaerobia se ve afectada significativamente por la temperatura.

Para los ensayos desarrollados se ha elegido la operación en condiciones **mesófilas** (35ºC), que es la más ampliamente empleada a escala real (mayormente, por cuestiones económicas y de tradición).

b) Inoculo

Dado que el proceso global de degradación anaerobia es complejo y requiere la presencia de distintos grupos de microorganismos, el origen y naturaleza del inoculo tiene una clara influencia en la cinética y niveles de degradación obtenidos.
Algunos inóculos referenciados para ensayos de biodegradabilidad son purines digeridos, mezcla de fangos o fangos adaptados. El que más comúnmente se usa, debido a su mayor disponibilidad y a la gran variedad de microorganismos que posee, es el

procedente de reactores anaerobios de plantas municipales que tratan fango primario o una mezcla de primario y secundario. En aquellas ocasiones en las que se traten residuos especiales y/o en condiciones especiales conviene utilizar un fango adaptado.
Moreno-Andrade y Buitrón (2004) estudiaron el efecto que tiene el origen de los microorganismos sobre los ensayos de biodegradabilidad, obteniendo que los resultados de biodegradabilidad variaron en función de la procedencia del inóculo, encontrándose una relación entre el grado de biodegradación y la actividad metanogénica específica: a mayor actividad metanogénica mejores resultados de biodegradación.

Se ha elegido trabajar con **fango mixto digerido** proveniente de la estación de tratamiento de aguas residuales de Valladolid, por disponibilidad y fiabilidad.

c) Relación sustrato / microorganismos (S_0/X_0)

El efecto de esta relación no se suele tener en cuenta en los protocolos normalizados existentes (Angelidaki et al. 2009), sin embargo los resultados de biodegradabilidad se ven fuertemente afectados con el valor de la relación sustrato/microorganismos. Se ha encontrado un efecto positivo en la relación So/Xo con la velocidad específica de producción de gas. Según Buitrón (2002), a mayores relaciones mayor velocidad específica de producción de biogás.

En el desarrollo de los ensayos se ha elegido una **relación sustrato/inoculo de 0.5 g SV/gSV** para todos los ensayos realizados.

d) Medio del ensayo

En el desarrollo de un ensayo de biodegradabilidad el medio debe de aportar a los microorganismos los elementos esenciales como los nutrientes, vitaminas y elementos traza necesarios a su crecimiento. La falta de algunos de los componentes esenciales puede ser un factor limitante en el crecimiento de los microorganismos y por eso falsear los resultados de biodegradabilidad. La presencia de oligoelementos y vitaminas en el medio favorecen la producción de biogás y mejoran los niveles de biodegradación obtenidos (Buitrón, 2002). La tabla siguiente presenta la disolución de los macronutrientes y de los elementos traza esenciales al medio.

Tabla 5.2 – Disolución de macronutrientes y elementos traza (Field et al. 1988)

Macronutrientes		**Disolución elementos traza**	
Sustancia	**Concentración (g/L)**	**Sustancia**	**Concentración (mg/L)**
KH_2PO_4	37	$FeCl_3 . 4 H_2O$	2.000
NH_4Cl	170	$CoCl_2 . 6 H_2O$	2.000
$CaCl_2. 2 H_2O$	8	$MnCl_2 . 4 H_2O$	500
$MgCl_2. 4 H_2O$	9	$CuCl_2 . 2 H_2O$	30
Na_2SO_4	49	$ZnCl_2$	50
		H_3BO_3	50
		$(NH_4)_6Mo_7O_{24} . 4 H_2O$	90
		$Na_2SeO_3. 5 H_2O$	100
		$NiCl_2 . 6 H_2O$	50
		EDTA	1.000
		Rezasurina	500
		HCl	1 mL/L

En los ensayos realizados durante la tesis se ha añadido **1 mL de la disolución** presentada en la tabla 5.2 por cada litro de inoculo.

e) <u>Número de réplicas</u>

La muestra de fango puede presentar alta heterogeneidad por lo que es conveniente distribuir el fango en cada ensayo de la manera más homogénea. A pesar de tomarse las precauciones adecuadas no siempre se evitan los problemas derivados de este hecho. Con el fin de minimizar los efectos y obtener resultados fiables es conveniente transferir el fango de manera aleatoria entre todos los ensayos y con la mayor mezcla posible. Por otra parte se recomienda la realización de ensayos por triplicado (ASTM D 5210 (1992), ISO 11734 (1995)).

Todos los ensayos realizados en la presente tesis se han realizado por **triplicado**.

f) <u>Validación del ensayo</u>

Es recomendable en este tipo de ensayos que se realicen ensayos de control con una sustancia de referencia, de forma que se compruebe la actividad del inóculo empleado.

Las sustancias a utilizar son compuestos fácilmente biodegradables como la celulosa, albúmina y trioleato de glicerol.

En los ensayos recogidos en esta tesis se han montado sucesivos **test de "control"**, con **celulosa como sustrato**.

5.2.5. Procedimiento para la realización de los ensayos BMP

El seguimiento experimental para la realización de los ensayos de biodegradabilidad se ha basado en protocolos existentes (Angelidaki et al. 2009, UNE-EN-ISO 11734, 1995), adaptando estos a las condiciones deseadas.

Como se ha presentado anteriormente (apartado 5.2.4), el inoculo es fundamental. Conviene que sea lo más fresco posible, pero que su producción de biogás endógena sea despreciable comparada con la exógena (debida al sustrato). Para minimizar la producción endógena es conveniente introducir el inóculo en una cámara caliente a 35ºC durante al menos 3 días antes de iniciar el ensayo. Este tiempo es suficiente para readaptar el lodo a la temperatura del ensayo en el caso de que hubiese sido almacenado a 4ºC para su conservación.

En todos los ensayos realizados para la determinación de la biodegradabilidad de un residuo (pre-tratado o no) se ha realizado en paralelo un test de biodegradabilidad del inóculo (sin adicionar sustrato), denominado "blanco". El objetivo de este blanco es cuantificar la producción debida solamente al cultivo, para restar la producción correspondiente al inóculo en los ensayos realizados a los residuos.

Como se ha indicado anteriormente, para verificar la reproducibilidad del ensayo se han realizado los ensayos por triplicado.

Los pasos clave que se han seguido para la realización de los ensayos BMP han sido:

1. Adición del volumen del inóculo calculado en el digestor (de forma que el volumen libre de la cámara de gas sea suficiente para el seguimiento de la producción de biogás)
2. Adición de una solución reductora (100 mg $Na_2S.9H_2O/L$) y una solución tampón (5 g $NaHCO_3/L$). La solución reductora tiene por función asegurar la ausencia de oxígeno en el medio durante todo el ensayo. La solución tampón se emplea para neutralizar los protones generados en la descomposición del sustrato, y mantener el pH del medio lo más constante posible. El cultivo debe de contener los nutrientes y elementos traza necesarios al correcto crecimiento de los microorganismos (1 mL/L) con la composición anteriormente descrita.
3. Ajuste de pH del medio a aproximadamente 7, empleando HCl o NaOH.
4. Adicción del sustrato a la concentración y relación S_0/X_0 deseadas (para evitar la acidificación del medio).
5. Después de sellar los digestores se procede al purgado del aire del sistema mediante la introducción de un gas inerte (helio, por ejemplo), favoreciendo la eliminación de oxígeno contenido en los botes y asegurando una atmósfera anaerobia desde el primer momento.
6. Preparados los digestores se colocan en una cámara caliente a la temperatura seleccionada para el ensayo (35ºC). Cuando estos obtengan la temperatura ambiente (aproximadamente 20 minutos) se da por iniciado el ensayo.
7. Durante el seguimiento de los ensayos se mide el incremento de presión y se analiza la composición de biogás (por cromatografía de gases).

El ensayo se da por terminado cuando la variación de presión durante los últimos días es inferior al 10% de la producción total de biogás, o se ha alcanzado la producción de biogás teórica esperada.

5.2.6. Equipo experimental

El sistema empleado se basa en la técnica manométrica con medida de la producción de biogás a partir del aumento de presión en un recipiente de volumen constante (“digestor”), y posterior medición por cromatografía gaseosa de la composición en metano del biogás.

Se describen a continuación las características del equipo:

Digestores utilizados

Como reactores se han utilizado dos tipos de botes, 2L y 250mL, fabricados en borosilicato transparente (Sigma-Aldrich). El empleo de uno u otro se ha realizado dependiendo de la naturaleza del residuo. Aquellos residuos con partículas de mayor tamaño (naranja, paja, bagazo) se han realizado en los botes de mayor tamaño.
La figura 5.5 presenta una imagen de los digestores utilizados.

Figura 5.5 – Digestores de borosilicato utilizados en los ensayos de biodegradabilidad

Sistema de agitación

Se han utilizado dos sistemas distintos de agitación. Para los botes de 2 L se ha utilizado un sistema rotatorio (Wheaton – Roller apparatus), mientras para los botes de 250 mL se utilizó un sistema de agitación shacker (New Brunswick Scientific, G10 – Gyrotory Shacker). Ambos sistemas se muestran en la figura 5.6.

Figura 5.6 – Equipos de agitación utilizados, rotatorio y shacker respectivamente.

Medida de presión

El transmisor de presión utilizado ha sido el ifm PN5007 con un rango de medición de 0 a 1bar, mostrado en la figura 5.7

Figura 5.7 – Transmisor de presión

5.2.7. Tratamiento de datos de los BMP

Producción de Biogás o de metano (mL CH_4)

Una vez finalizado el ensayo, los datos de las lecturas de presión se transforman en volumen de biogás generado.

El cálculo teórico se basa en la ley de los gases ideales y en la suposición de que la solubilidad del metano en el medio es despreciable.

El aumento de la presión se relaciona con un aumento en el número de moles del sistema,

$$\Delta P.V_{cámara\ de\ gas} = \Delta n.R.T_{ensayo} \rightarrow \Delta n = \frac{\Delta P.V_{cámara\ de\ gas}}{R.T_{ensayo}} \qquad (5.3)$$

siendo

ΔP = variación de la presión durante el ensayo (atm)

$V_{\text{cámara de gas}}$ = volumen libre de la cámara de gas (dm^3)

Δn = variación en el número de moles de gas generados (mol)

R = contantes de los gases ideales (atm.dm^3/mol.K)

T_{ensayo} = temperatura del ensayo (K)

Cuando la cantidad de gas generado es conocida, se puede relacionar con el volumen que ocuparía a una temperatura presión y presión (0ºC y 1 atm)

$$\Delta V.P^0 = \Delta n.R.T^0 \rightarrow \Delta V = \frac{\Delta n.R.T^0}{P^0} \qquad (5.4)$$

siendo

P^0 = presión de referencia (1 atm)

T^0 = temperatura de referencia (273K)

ΔV = producción de biogás, a 0ºC y 1 atm durante el ensayo (dm^3)

Sustituyendo el valor de Δn de la ecuación 5.3 en 5.4, tenemos

$$\Delta V = \frac{V_{cámara\ de\ gas} \cdot T^0}{P^0 . T_{ensayo}} . \Delta P = c\ \Delta P \qquad (5.5)$$

Los valores de volumen de cámara de gas, T_{ensayo}, presión de referencia y temperatura de referencia son constantes por lo que se pueden agrupar dando lugar a la contante *c*.

Con el análisis de la composición de biogás, es posible cuantificar la cantidad de metano producido,

$$\Delta V_{metano} = \Delta V . M \qquad (5.6)$$

siendo

M = Fracción molar del metano en el biogás generado
ΔV = producción de metano, a 0ºC y 1 atm durante el ensayo (dm^3)

Para conocer la producción real de biogás debida al sustrato, a la producción total que se haya obtenido se le resta la producción debida solamente al ensayo en “blanco” (test solo con inóculo).

A continuación se presentan unas gráficas como ejemplo, en las que se recogen las curvas de producción de biogás total (obtenido en un ensayo a un sustrato cualquiera) y del blanco (correspondiente al test con inóculo). La curva de producción real se obtiene como diferencia de las anteriores.

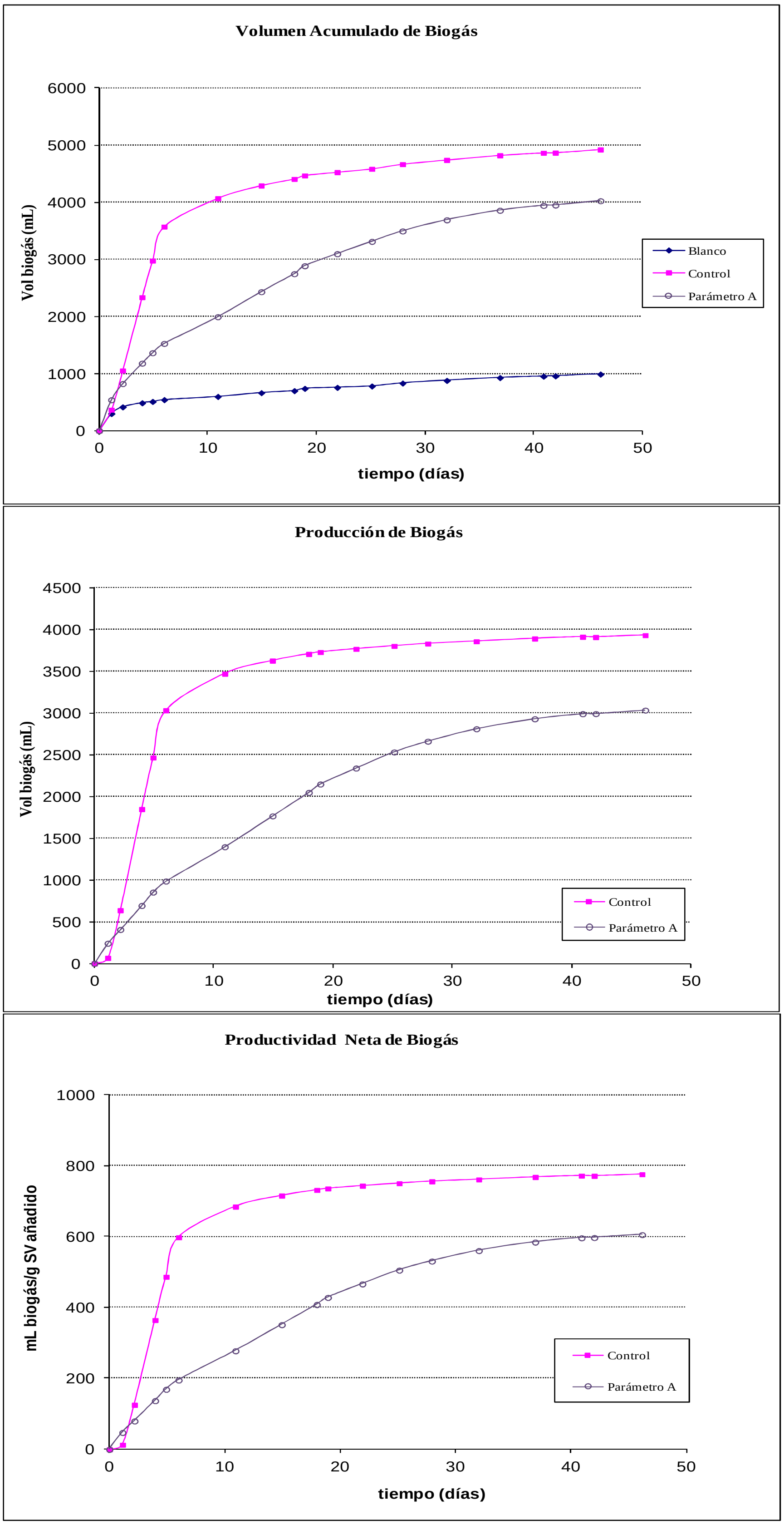


Figura 5.8. Ejemplo de cálculo de productividad de biogás

A partir del valor de producción de biogás o metano (mL) se calcula la **productividad** del residuo, dividiendo este valor con respecto a los gSV de residuo introducido al ensayo (gSV añadido). De este modo se obtiene el resultado final de productividad como: **mL biogás/g SV$_{\text{añadido}}$** y **mL CH$_4$/g SV$_{\text{añadido}}$**.

5.3. Parámetros clave: operación y respuesta

5.3.1. Parámetros de operación: Factor de Severidad (log R$_0$)

En el tratamiento de hidrólisis térmica, la temperatura y el tiempo de operación determinan las condiciones de severidad del pre-tratamiento que pueden ver presentadas según el parámetro log R$_0$ (Hendriks and Zeeman, 2009), donde

$$\log R_0 = \log\left(t.exp\left(\frac{T-100}{14.75}\right)\right) \qquad (5.7)$$

Siendo t el tiempo en minutos, T la temperatura en ºC, 100 es la temperatura base de 100ºC y 14.75 es la energía de activación asumiendo que la reacción de hidrólisis y toda la conversión es de primer orden.

La tabla 5.4 muestra, como ejemplo, una serie de factores de severidad que corresponden a distintas combinaciones de temperatura (T) y tiempo (t) de operación.

Tabla 5.4. Factores de severidad correspondientes a distintas condiciones de operación

T (ºC)	t (min)	log R0
0	0	0,00
100	5	0,70
100	15	1,18
120	15	1,76
120	30	2,07
150	5	2,17
150	15	2,65
150	30	2,95
170	15	3,24
170	30	**3,54**
180	5	3,05
180	30	3,83
200	2	3,25
200	5	3,64
220	1	**3,53**
220	5	4,23
220	15	4,71

Se observa que un mismo factor de severidad puede corresponder a dos combinaciones temperatura-tiempo diferentes. Así, por ejemplo, un factor de severidad de 3.5 corresponde a 170ºC - 30 min y a 220ºC – 1 min.

5.3.2. Parámetros de respuesta: Factor de Biodegradabilidad (FB)

Dado que el objetivo que se busca es mejorar la productividad del residuo tratado frente al no tratado, el parámetro de respuesta clave empleado en la presente tesis es la relación entre ambos, definido como **factor de biodegradabilidad (FB)**.

Por tanto, el factor de biodegradabilidad es la relación entre la productividad obtenida en los ensayos alimentados con residuo pre-tratado frente al control alimentado con residuo no pre-tratado.

$$FB = \frac{\left({mL\ CH_4}/{gSV_{añadido}} \right)_{Hidrolizado}}{\left({mL\ CH_4}/{gSV_{añadido}} \right)_{No-Hidrolizado}} \qquad (5.8)$$

De este modo:

- FB>1 → mejora de la biodegradabilidad con respecto al no-hidrolizado
- FB<1 → empeoramiento de la biodegradabilidad con respecto al no-hidrolizado

5.4. Métodos Analíticos

Para el desarrollo de la tesis ha sido necesario conocer una serie de parámetros para la caracterización de las muestras, tanto del inoculo como del sustrato. Su determinación se realizó mediante las técnicas analíticas propuestas por *Standard Methods for the examination of water and wastewater* (APHA, 2005).

A continuación se describen de forma breve las técnicas analíticas usadas.

5.4.1. pH

La determinación electrométrica del pH se basa en la medida de la actividad de los iones de hidrógeno por mediciones potenciométricas utilizando un electrodo indicador de vidrio, otro de referencia y tampones de pH 4 y 7.

La fuerza electromotriz (fem) producida en el sistema de electrodo de vidrio varía linealmente con el pH y esta relación se describe comparando la fem medida con el pH de diferentes tampones. El pH de la muestra se determina por extrapolación.

La temperatura afecta la medida del pH de dos formas, efectos mecánicos producidos por cambios en las propiedades de los electrodos y efectos químicos causados por cambio de equilibrio. De esta forma es conveniente proceder a la medida del pH de la muestra siempre a la temperatura ambiente.

El medidor de pH utilizado consta de un potenciómetro, con lectura de temperatura y compensación de la misma, un electrodo combinado de vidrio (crison 52-02 de pH de 0-14) y una sonda (crisol C.A.T. Pt1000) para compensar la temperatura. Para muestras de fangos, sólidas y semi-sólidas se usa un electrodo de penetración (crison 50-53 con intervalo de temperatura de 0-45ºC)

5.4.2. Sólidos totales y sólidos volátiles (ST y SV)

El análisis de sólidos es un parámetro bastante importante en el control de procesos físicos y biológicos, en la caracterización de efluentes y lodos, en la eficiencia de procesos de tratamientos, entre otros.

En la determinación de los ST y SV se ha seguido el *Standard Methods for the examination of water and wastewater* (APHA, 2005) – Referencia 2540, con algunas modificaciones.

Equipos necesarios: Balanza analítica, estufa y mufla

Material: Capsula, espátula

Inicialmente hay necesidad de preparar la capsula donde se va a proceder al análisis de la muestra. Si en la medición se pretende analizar SV (i), se debe incinerar la capsula a 550 ± 50ºC por al menos 1 hora en una mufla. Sí por lo contrario, solamente se pretende hacer el análisis de los ST (ii), de debe calentar la capsula a 103-105ºC por al menos 1 hora en una estufa.

Después de preparada la capsula se debe de conservar en un desecador y pesar inmediatamente antes de usar (p_0)

Análisis de la muestra

1 – Elegir una cantidad de muestra que proporcione un residuo entre 25 a 50g,

2 – Transferir la cantidad de muestra bien mezclada a la capsula previamente preparada y pesada (opciones i o ii), (p_m)

3 – Secar la capsula con la muestra durante al menos 1 hora en una estufa a 103-105ºC,

4 – Enfriar la capsula en un desecador para equilibrio de temperatura y pesar en balanza analítica (p_1)

Repetir el ciclo 3 / 4 hasta obtener una de las condiciones: a) peso constante, b) la pérdida de peso sea menor de 4% del peso inicial, c) la pérdida de peso sea menor de 0.5 mg del peso inicial. Elegir la menor de ambas y valorar los ST

5 – Incinerar la capsula con la muestra a 550 ± 50ºC en una mufla, hasta peso constante,

6 – Enfriar la capsula en un desecador para equilibrio de temperatura y pesar en una balanza analítica (p_2).

Repetir el ciclo 5 / 6 hasta obtener una de las condiciones: a) peso constante, b) la pérdida de peso sea menor de 4% del peso inicial. Elegir la menor de ambas y valorar los SV.

A continuación se presentan las ecuaciones necesarias para el cálculo

p_0 = peso capsula (g)
p_m = peso muestra original + capsula (g)
p_1 = peso residuo seco + capsula (g)
p_2 = peso residuo incinerado + capsula (g)

$$ST\ (g/kg) = \frac{(p_1 - p_0) * 1000}{p_m - p_0} \qquad (5.9)$$

$$SV\ (g/kg) = \frac{(p_1 - p_2) * 1000}{p_m - p_0} \qquad (5.10)$$

5.4.3. Demanda Química de Oxígeno para sólidos (DQO$_{\text{sólidos}}$)

La Demanda Química de Oxígeno puede considerarse una medida aproximada de la demanda teórica de oxígeno, que es la cantidad de oxígeno consumido para la oxidación total de los compuestos orgánicos a productos inorgánicos.

El método utilizado se basa en el método de Reflujo abierto según la norma UNE 77004:2002 y adaptando el método seguido por *Standard Methods for the examination of water and wastewater* (APHA, 2005). Es aplicable para valores de DQO entre 30 mg/L y 19000 mg/L, no siendo aplicable en muestras que tras su dilución contienen más de 2000 mg/L de iones cloruro.

Reactivos necesarios:

- Solución catalítica (10 g/L): Disolver 25g de $AgSO_4$ en 2.5L de H_2SO_4 96% y 1.84 g/mL.
- Solución digestora (0.2M): Disolver 117.68g de $K_2Cr_2O_7$ (previamente secado en a 105ºC por 2 horas) en 750 mL de agua Elix, añadir 17g $HgSO_4$ e incorporar poco a poco 500 mL de H_2SO_4 concentrado. Una vez frio diluir hasta 2000 mL en un matraz aforado.
- Solución FAS (200 g/L): Disolver 400g de $Fe(NH_4)_2(SO_4)_2.6H_2O$ en 1000 mL, añadir 80 mL de H_2SO_4 concentrado. Dejar enfriar e diluir hasta 2000 mL en un matraz aforado.
- Solución patrón dicromato de potasio (1N, 0.166 mol/L)
- Solución patrón hidrogeno ftalato de potasio

Procedimiento y preparación de muestras

La muestra se lleva a ebullición con reflujo en presencia de sulfato de mercurio (II), de una cantidad conocida de dicromato de potasio y de un catalizador de plata en medio fuertemente acidificado por ácido sulfúrico durante 2 horas a 150ºC. Después de la digestión, el dicromato no reducido se determina por valoración con sulfato de amonio ferroso. El valor de la DQO se determina a partir del dicromato reducido, el equivalente a la cantidad de materia oxidada.

- Ensayo blanco: se debe realizar un ensayo en blanco al mismo tiempo que la determinación de las restantes muestras, donde se sigue el mismo procedimiento operatorio pero reemplazando la muestra por 10 mL de agua Elix.
- Equipo de digestión: se usa un equipo de digestión de 6 a 12 unidades con tubos de digestión de 42 mm de diámetro con boca esmerilada. Programar la temperatura a 151ºC y tiempo de digestión de 120 min.
- Digestión de las muestras: Para las muestras utilizadas, muestras sólidas, se pesó una cantidad representativa (1-1.5g) con respuesta dentro del rango a la que se añadió 10 mL de agua Elix.

Colocar en el suporte los tubos de digestión previamente lavados con agua Elix y secos, incorporar a los tubos la porción de ensayo y 2/3 bolitas controladores de ebullición. Se debe reservar un tubo para el ensayo en blanco. Dosificar lentamente 20 mL de solución digestora y 30 mL de solución catalítica, agitando cuidadosamente el tubo de digestión tomando en cuenta que el proceso es exotérmico. Llevar las muestras a la campana extractora y conectar el equipo a la temperatura y tiempo de digestión. Una vez terminada la digestión, dejar las muestras enfriar a la temperatura ambiente, quitar los tubos de digestión y trasvasar el digerido a un matraz de 500 mL. Se deben lavar las paredes del tubo varias veces con pequeñas cantidades de agua. Añadir agua Elix hasta el enrase de 500 mL con el objetivo de diluir el color permitiendo observar el viraje de color durante el proceso de valoración del dicromato no reducido.

- <u>Normalización del FAS</u>: Es necesario calcular la normalización del FAS antes de cada serie de valoraciones. Se debe para ello, colocar 10 mL de solución patrón de dicromato potásico 1N en un matraz de 500 mL, añadir 30 mL de sulfúrico concentrado y diluir hasta enrase del volumen del matraz con agua Elix. Añadir 10 gotas de ferroína y valorar. Anotar el volumen de FAS consumido.
- <u>Valoración</u>: Añadir 10 gotas de indicador ferroína a cada matraz (la cantidad del indicador debe de permanecer constante). Mediante agitación magnética moderada, titular el exceso de dicromato con FAS hasta cambio de viraje (de naranja – verde claro que vira a verde oscuro y luego continuar valorando hasta verde – gris mate). Anotar volumen de FAS consumido.
- <u>Criterio de aceptación:</u> En cada ensayo se determina el valor de DQO de un patrón como control de exactitud y un duplicado como control de precisión. Se considera satisfactorio el ensayo en el caso de que el valor experimental es, como mínimo, 96% el valor teorico.

A continuación se presentan las ecuaciones necesarias para el desarrollo de los cálculos

a – volumen de FAS utilizado en la valoración del blanco (mL)
b – volumen de FAS utilizado en la valoración de la muestra (mL)
N – normalidad del FAS
V_{FAS} – volumen consumido en la valoración del FAS (mL)
g_m – masa de muestra digeridos (g)

$$N_{FAS} * V_{FAS} = N_{K_2Cr_2O_7} * V_{K_2Cr_2O_7} \qquad (5.11)$$

$$DQO\ (mg\ O_2/g) = \frac{(a-b)*8*N}{g_m} \qquad (5.12)$$

5.4.4. Nitrógeno Kjeldahl (NKT)

Cuando el nitrógeno orgánico y el amoniacal se determinan conjuntamente, se denomina de *nitrógeno Kjeldahl*. Si se determina individualmente el kjeldahl y el amoniacal, se puede obtener el nitrógeno orgánico por diferencia.

El método utilizado se basa en la totalidad con el método seguido por *Standard Methods for the examination of water and wastewater* (APHA, 2005) – Referencia 4500 - N_{org}.

Reactivos necesarios:

- Solución de bórico: Disolver 40g de ácido bórico en agua y añadir 20 mL de indicador mixto y diluir hasta 200 mL.
- Solución indicador mixto: Disolver 200 mg de rojo de metilo en 100 mL de etanol. Disolver 100 mg de azul de metileno en 50 mL de etanol. Mezclar ambas disoluciones.
- Solución madre ácido sulfúrico 1N: Disolver 27.8 mL de ácido sulfúrico al 96%, dejar enfriar y llevar a matraz de 1000 mL.

- Solución patrón de hidrógeno ftalato de potasio: Pesar 0.3 g de ftalato previamente secado a 105ºC durante una hora, y llevar a matraz de 50 mL.
- Solución de sosa caustica 6N: Pesar en una jarra de plástico 480 g de sosa caustica y disolver en 2L de agua.
- Solución de NaOH 0.5N: Disolver en un vaso de plástico, 10 g de lentejas de NaOH en un volumen de 400 mL. Dejar enfriar y llevar a un matraz de 500 mL.
- Solución de NaOH 0.03N: Diluir en un matraz de 250 mL, 15 mL de NaOH 0.5N. Diluir hasta volumen total.
- Solución de ácido sulfúrico 0.1N; 0.05N; 0.02N
- Catalizador Kjendahl: Cu 0.3% - $CuSO_4.5H_2O$

Procedimiento y preparación de muestras

El método se basa en el siguiente principio: En la presencia de sulfúrico y un catalizador a una temperatura controlada de 370ºC el nitrógeno se transforma en sulfato de amonio. El amoniaco se destila en medio alcalino y se absorbe en ácido bórico, el amoniaco se determina por titulación con ácido sulfúrico de concentración normalizada frente a patrón.

- Tratamiento de muestras: Las determinaciones sobre muestra seca no son exactas porque el secado origina pérdidas de sales de amonio. Para muestras de fangos y sedimentos, pesar una porción representativa (0.5 – 1g), transferir a un tubo de digestión y añadir 25 mL de agua. Sí la muestra tiene sólidos macroscópicos o material insoluble, se debe de homogeneizar.
- Digestión: En el caso de muestras sólidas, a la cantidad previamente pesada (0.5 – 1g), añadir 10 mL de agua y 3 mL de ácido sulfúrico, remover con precaución y esperar 2 minutos. Pasado el tiempo añadir nuevamente 3 mL de ácido sulfúrico, la solución digestora, el catalizador y unas bolitas de dieléctrico para evitar sobrecalentamiento. Colocar los digestores a 370ºC durante 60 minutos. Finalizado el tiempo de digestión, dejar enfriar los tubos y proceder a destilar el digerido.

- Destilación: Seguir las instrucciones del equipo de destilación – destilador Büchi. Dosificar agua e hidróxido sódico, recoger el destilado en un matraz de 100 mL de bórico indicador. Para muestras sólidas, se enlazan 2 programas; un predestilado (25 mL de agua, 15 mL de NaOH, dosificar los 100 mL de bórico-indicador y esperar 5 segundos) seguido de un programa de destilado (5 mL de agua, 15 mL de NaOH, 5 segundos de espera y destilación con corriente de vapor durante 10 minutos).
- Valoración: Valorar el destilado con ácido sulfúrico de concentración conocida hasta cambio de color (de verde a morado brillante). Anotar el volumen consumido.
- Criterio de aceptación: Para cada serie se determina el valor de NKT de un patrón (triptófano 13% N) como control de exactitud y un duplicado como control de precisión. Se considera satisfatorio el ensayo cuyo valor experimental sea como minimo el 96% del valor teorico.

A continuación se presentan las ecuaciones necesarias para el desarrollo de los cálculos

N – normalidad del sulfúrico utilizado en la valoración
V – volumen de sulfúrico consumido en la valoración (mL)
m_m – masa de muestra que se ha digerido (g)

$$NKT(mg\,N/kg) = \frac{(N * V).14000}{m_m} \qquad (5.13)$$

5.4.5. Carbono orgánico total (TOC)

El método utilizado se basa en el método de combustión – infrarrojo. El método utilizado se basa en la totalidad con el método seguido por *Standard Methods for the examination of water and wastewater* (APHA, 2005) – Referencia 5310.

Se trata de un método utilizado para una gran diversidad de muestras, pero su exactitud depende de la reducción del tamaño de partícula. En ese caso, se debe de utilizar para muestras con concentración de carbono orgánico total superiores a 1 mg/L.

Equipos necesarios: Analizador de carbono orgánico total (TOC), equipo TOC-5050 (modulo líquidos), SSM-5000 (modulo para sólidos) - SHIMADZU

Reactivos y material utilizados:

- Disolución patrón carbono total (TC) de biftalato de potasio anhidro $C_8H_5KO_4$ (Mm 204.23 g/mol y 99.5%): Preparar una solución madre de 1000 ppm para calibración y como control de calidad. Pesar exactamente 2.125 g secados en estufa durante 2 horas a 105ºC y llevar a un matraz aforado de 1000 mL. La disolución se debe conservar a 4ºC para su estabilidad.
- Disolución patrón mixto carbono inorgánico (IC) de carbonato de sodio anhidro Na_2CO_3 y bicarbonato de sodio anhidro $NaHCO_3$: Preparar una disolución madre mixta de 1000 ppm. Pesar exactamente 4.41g y 3.50g respectivamente y llevar a un matraz de 1000 mL. La disolución se debe conservar a 4ºC para su estabilidad.
- Disolución patrón de nitrógeno total (TN) de cloruro amónico NH_4Cl: Preparar una disolución de 100 ppm. Pesar 0.3821 g y llevar a un matraz de 1000 mL.
- Patrón de D-glucosa anhídra $C_6H_{12}O_6$
- Gas portador oxigeno purificado libre de CO_2 (Linde oxigeno 5.0, $N_2 < 5$ ppm/V)
- Gas portador aire sintetico alta pureza.
- Cubetas de cerámica y lana cerámica: sumergir en HCl 2N, lavar y calcinar a 550ºC.

Procedimiento y preparación de muestras:

El método se basa en el siguiente principio: para determinar la cantidad de carbono orgánico, las moléculas orgánicas deben romperse en unidades de carbono simples en una cámara de combustión a la temperatura adecuada dependiendo de la fracción de carbono a determinar. En presencia de un catalizador, la muestra se quema y se descompone en CO_2 que puede medirse directamente en un analizador de infrarrojo no disperso. La señal analógica de salida del detector genera un pico cromatográfico proporcional a la concentración de TC de la muestra.

Las moléculas monoatómicas como el N_2, O_2 y H_2 no absorben radiación infrarroja, mientras que las moléculas poliatómicas tales como el CO_2 y CH_4 absorben radiación infrarroja a diferentes longitudes de onda según la condición de adherencia y los tipos de átomos que constituyen la molécula. La cantidad de rayos infrarrojos absorbidos es proporcional a la densidad del CO_2 según la ley de Lambert- Beer.

- Calibración del módulo de sólidos: Se ajusta la temperatura del horno a 900ºC de forma a permitir una correcta oxidación por combustión. Se elabora una recta de calibrado para TC y otra para IC con cuatro niveles de concentración. Se usa D-glucosa anhidra como patrón para TC y carbonato de sodio para IC. Las respuestas se obtienen en % peso.
- Ensayo blanco: Se realiza un ensayo con agua MiliQ
- Muestras sólidas: La muestra debe de ser representativa y estar bien pulverizada, pero como pesada máxima considerar 1 g de muestra.
- Procedimiento – Módulo de sólidos: Pesar una cubeta de cerámica previamente calcinada a 550ºC y añadir una cantidad de muestra homogénea y representativa (máximo 1g). Tratándose de una muestra solida se debe recubrir con algodón absorbente (previamente calcinado) de forma a evitar proyecciones al introducir la muestra en el horno (no se debe recubrir para mediciones de CI)

Cuando una muestra que contiene materia orgánica, materia mineral carbonosa (carbonatos, bicarbonatos, carburos, etc) y materia mineral no carbonosa, se somete a combustión total a 900ºC, todo el carbono presente se transforma en anhídrido carbónico el cual puede ser analizado cuantitativamente. Si esa misma muestra es sometida a 200ºC y a la acción de un ácido (H_3PO_4 a 25%), se genera igualmente CO_2 pero solamente proveniente de la materia inorgánica carbonosa.

En el caso de la combustión total a 900ºC, se obtiene el resultado del carbono total (TC), mientras en el segundo caso, se obtiene el carbono inorgánico (IC). El valor del TOC es dado por la diferencia de ambos resultados según la ecuación,

$$TOC = TC - IC\ (\%peso) \qquad (5.14)$$

Capítulo 6

Resultados y Discusión

Apartado 6.1

Hidrólisis térmica de bagazo de cerveza

6.1.1. Introducción

La industria cervecera se considera la quinta industria más productora del mundo, pudiendo considerarse el valor de 23 litros/persona.año como un consumo medio.

La cebada, materia prima en el proceso de producción de cerveza, es hoy en día el cereal más abundante después del trigo, el maíz y el arroz.

En el proceso de elaboración de cerveza se generan una serie de residuos, como el bagazo, bagazo de lúpulo, levadura y tierras de filtración (Mussatto et al. 2006; Fillaudeau et al. 2006), así como agua residual.

En concreto, el bagazo de cebada representa un residuo importante para la industria cervecera, cuyo destino habitual es la alimentación animal. Sin embargo, su elevada generación conduce a la necesidad de buscar tratamientos o alternativas.

La digestión anaerobia se plantea como una excelente alternativa dado que permite la recuperación energética mediante la producción de biogás (Tewelde et al. 2012). Sin embargo, como residuo lignocelulósico se trata de una compacta estructura de celulosa (37.6%), hemicelulosa (34.9%) cerrada por lignina (15.8%) (Sun et al. 2005), y por tanto la etapa de hidrólisis resulta limitante para el proceso anaerobio.

La aplicación de una etapa previa de pre-tratamiento permitirá que las macromoléculas se conviertan en material más accesible a las bacterias anaerobias.

En el presente capítulo, se recoge el estudio realizado a bagazo de cervecera, sometido a un pre-tratamiento de hidrólisis térmica con explosión de vapor. La evaluación del efecto del pre-tratamiento se ha realizado mediante ensayos de potencial metanogénico.

6.1.2. Material y Métodos

La metodología seguida y el equipo empleado se han descrito previamente en el capítulo 5 de “Materiales y Métodos” (apartados 5.1.1 y 5.2.5). A continuación se recogen únicamente algunos datos concretos relativos al pre-tratamiento y los ensayos de potencial metanogénico.

a) Pre-tratamiento:

- Dispositivo experimental: La planta empleada corresponde al piloto Cambi® descrito en el apartado 5.1.1.

- Condiciones de operación: Se recogen en la tabla 6.1.2 (temperatura y tiempo). Se observa que la temperatura se estudió en el rango 150-220ºC y el tiempo se fijó en 1, 5 y 15 min. Estos valores conducen a factores de severidad (log R_0, calculados con la ecuación 5.7) en el rango 1-5.

b) Ensayos BMP

- Sustrato: bagazo de cervecera procedente de Heineken SA, fábrica de Madrid.

- Inoculo: Fango mixto digerido procedente de la estación de tratamiento de aguas residuales de Valladolid con una concentración de 12 g SV/kg.

c) Caracterización inicial del residuo

La tabla 6.1.1 muestra la caracterización inicial de la muestra de bagazo de cerveza empleada.

Tabla 6.1.1 – Caracterización de la muestra original para de bagazo de cerveza

Parámetro		Valor	Unidades
Sólidos Totales	ST	222.4±1.3	g/kg
Sólidos Volátiles	SV	215.1±1.3	g/kg
Porcentaje de SV	% SV	97	---
Demanda Química de Oxigeno	DQO	311621±19000	g O_2/kg
Razón DQO/SV	DQO/SV	1.45	---
Nitrógeno Kjendahl	NKT	10506	mg N/kg
Carbono orgánico total	TOC	11.66±0.75	% peso
Relación C/N	C/N	11.10	---

d) Planteamiento experimental

La tabla 6.1.2 muestra las doce combinaciones de temperatura-tiempo ensayadas.

e) Parámetros de respuesta

Como parámetros de respuesta al pre-tratamiento, se han utilizado el factor de severidad y el factor de biodegradabilidad descritos previamente en el capítulo 5 de “Materiales y Métodos” como ecuaciones 5.7 y 5.8.

Factor de Severidad (log R_0)

$$\log R_0 = \log\left(t.exp\left(\frac{T-100}{14.75}\right)\right) \qquad (5.7)$$

Factor de Biodegradabilidad (FB)

$$FB = \frac{\left({}^{mL\,CH_4}\!/_{gSV_{añadido}}\right)_{Hidrolizado}}{\left({}^{mL\,CH_4}\!/_{gSV_{añadido}}\right)_{No-Hidrolizado}} \qquad (5.8)$$

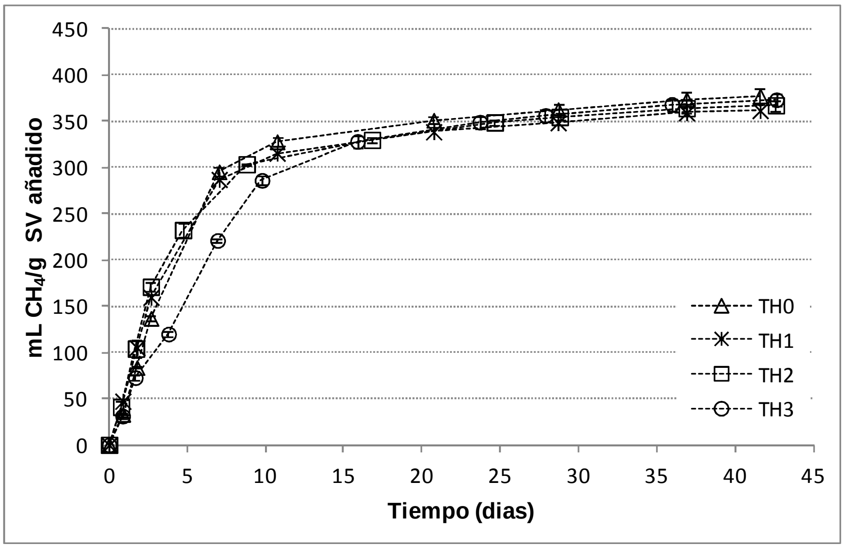
6.1.3. Resultados y Discusión

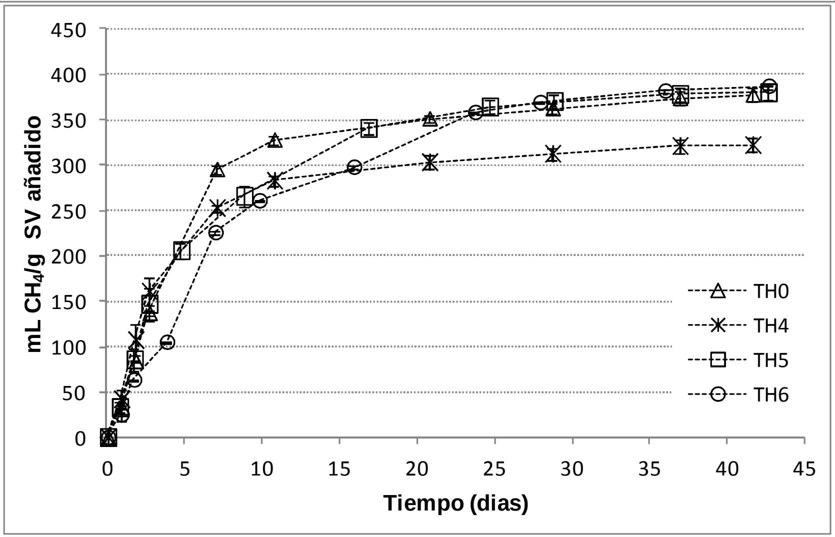
La tabla 6.1.2 muestra para las doce combinaciones de temperatura-tiempo (TH1-TH12) los resultados obtenidos, tanto de productividad (calculados según descrito en el apartado 5.3) como en factor de biodegradabilidad (FB descrito en la ecuación 5.8). Dicho factor ha sido calculado con respecto al correspondiente bagazo no tratado térmicamente (TH0).

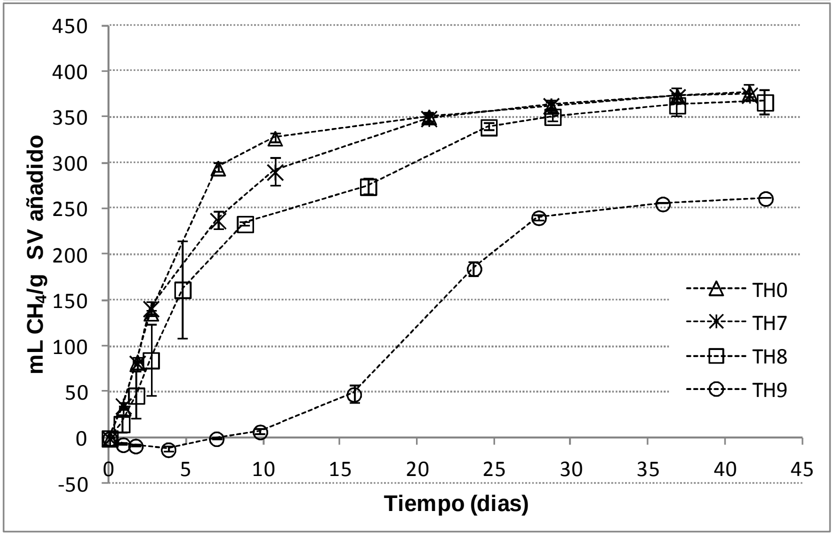
Tabla 6.1.2 – Condiciones de pre-tratamiento y parámetros de respuesta

Thi	**Tsat (ºC)**	**t (min)**	**logR0**	**mL CH4 / gSV (30 días)**	**FB (30 días)**
TH0	No tratado		0,00	362 ± 8	1,00
TH1	150	1	1,47	348 ± 0	0,96
TH2		5	2,17	355 ± 4	0,98
TH3		15	2,65	356 ± 7	0,98
TH4	170	1	2,06	313 ± 7	0,86
TH5		5	2,76	370 ± 8	1,02
TH6		15	3,24	369 ± 1	1,02
TH7	200	1	2,94	363 ± 3	1,00
TH8		5	3,64	351 ± 5	0,97
TH9		15	4,12	241 ± 3	0,67
TH10	220	1	3,53	345 ± 6	0,95
TH11		5	4,23	257 ± 21	0,71
TH12		15	4,71	164 ± 4	0,45

La figura 6.1.1 presenta la evolución de los ensayos BMP correspondientes.


mL CH4/g SV añadido
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
25
30
35
40
45
Tiempo (dias)
TH0
TH1
TH2
TH3


mL CH4/g SV añadido
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
25
30
35
40
45
Tiempo (dias)
TH0
TH4
TH5
TH6


mL CH4/g SV añadido
450
400
350
300
250
200
150
100
50
0
-50
0
5
10
15
20
25
30
35
40
45
Tiempo (dias)
TH0
TH7
TH8
TH9

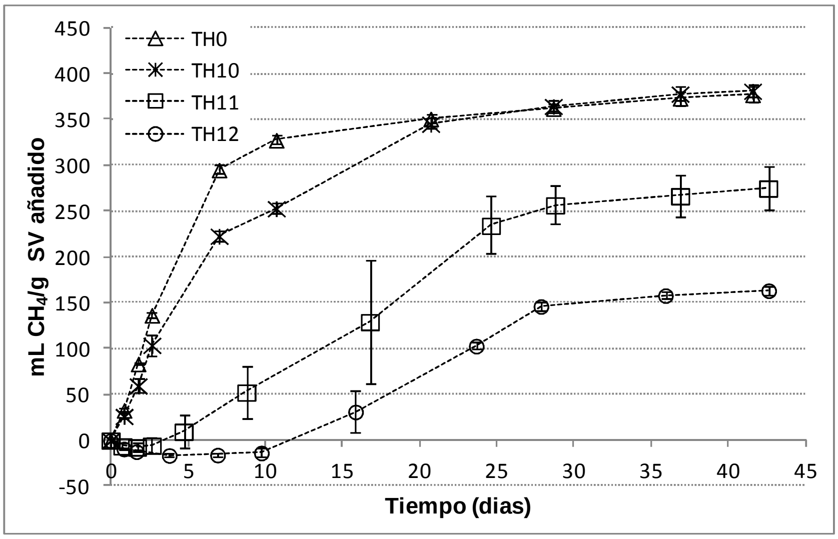


Figura 6.1.1 – Productividad en metano (mL CH_4/g $SV_{añadido}$)

A la vista de los resultados, la primera conclusión clara es que ninguno de los tratamientos realizados ha conducido a una mejora en la biodegradabilidad del bagazo de cerveza.

Por lo contrario, algunos tratamientos han conducido a un empeoramiento en su digestibilidad (tanto desde el punto de vista de la productividad final como de cinética). En concreto, los tratamientos TH9, TH11 y TH12 han disminuido notablemente el valor final de productividad de metano, dando lugar a una fase de retardo inicial de hasta 10 días, y a una pendiente de producción (cinética) inferior a la del bagazo original (TH0)

En la figura 6.1.2 se presenta el factor de biodegradabilidad (FB) frente al factor de severidad (log R_0). Esta figura pone claramente de manifiesto que para valores de severidad superiores a 3.50 el pre-tratamiento influye negativamente en la productividad del metano, obteniéndose valores inferiores al control TH0, decrecientes a mayor severidad.

Estos resultados coinciden cualitativamente con los obtenidos en la investigación con ultrasonidos realizada por Sapci (2013), en que la biodegradabilidad tras el tratamiento de sonicación fue menor que la inicial, y peor cuanto mayor energía aplicada.

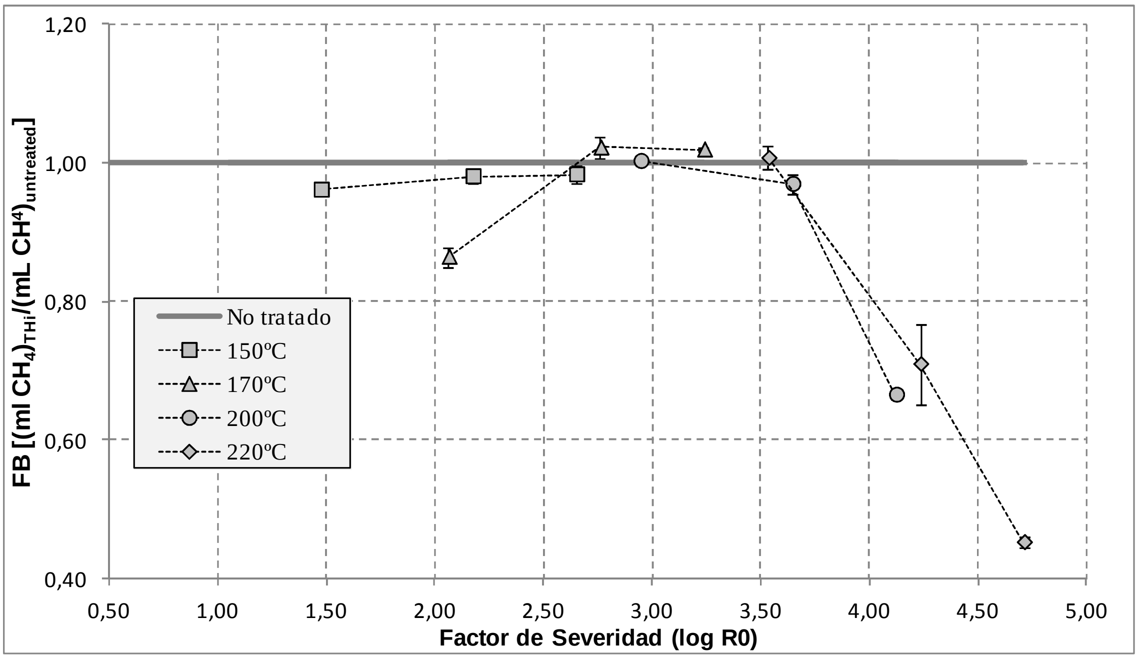


Figura 6.1.2 - Relación Factor de biodegradabilidad (FB) con el factor de severidad (log R_0) para los pre-tratamientos de hidrólisis aplicados a bagazo de cerveza

6.1.4. Conclusión

La hidrólisis térmica en las condiciones estudiadas (150-220ºC, 1-15 min) no ha resultado un tratamiento adecuado como etapa previa a la digestión de bagazo de cerveza, dado que no mejora la biodegradabilidad, ni en productividad ni en cinética. Por el contrario, en los tratamientos realizados en un factor de severidad superior a 3.50 se produjo un empeoramiento del proceso de digestión posiblemente debido a la formación de compuestos inhibitorios o recalcitrantes durante el pre-tratamiento que pueden influir negativamente en el proceso anaerobio.

6.1.5. Referencias

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Apartado 6.2

Hidrólisis térmica de cáscara de naranja

6.2.1. Introducción

El zumo de naranja es hoy en día una de las bebidas más consumidas, lo que lleva a que el cultivo de naranjas sea una de las mayores industrias en los Estados Unidos y en los países mediterráneos, representando una componente muy fuerte en la economía española (Faostat, 2010).

Adicionalmente a la producción de zumo, aproximadamente 50-60% de la materia prima se transforma en residuo (cáscara, piel, semillas, entre otros) (Wilkins et al. 2007).

Para reducir los problemas ambientales el residuo formado debe de ser procesado correctamente. Hasta muy recientemente el residuo de las naranjas era utilizado como alimento de ganado o simplemente quemado (Lapuerta et al. 2008). La situación actual tanto en producción como en legislación conduce a buscar alternativas.

La digestión anaerobia constituye una alternativa viable y muy interesante para el tratamiento y valorización del residuo generado, tanto desde el punto de vista medioambiental como energético (valorización). El tratamiento anaerobio actualmente se emplea con éxito con residuos orgánicos urbanos (basura municipal y lodos de depuradora), agrícolas e industriales ya que se trata de materia orgánica con elevadas características biodegradables (Chen et al. 2008).

Sin embargo, el residuo generado por la cáscara de naranja contiene aceites esenciales (90% D-Limoneno), que es conocido como un agente antimicrobiano, y por tanto puede causar inhibiciones en los digestores (Wilkins, 2009; Boluda-Aguilar et al. 2010). Los aceites esenciales son empleados en la industria cosmética y en medicina, por lo que su extracción se plantea como un estudio viable (Braddock et al. 1986; Boluda-Aguilar et al. 2010).

La digestión anaerobia de un residuo sólido como la naranja, está limitada por la etapa de hidrólisis (según se ha explicado en el capítulo 3 de “Antecedentes Específicos”) por lo que una etapa de pre-tratamiento ayudaría a que las macromoléculas resulten más accesibles a los microorganismos, facilitando su digestión. Por otro lado, algunas investigaciones (Boluda-Aguilar et al. 2010 y Wilkins, 2009) han concluido que después del pre-tratamiento de hidrólisis térmica a 150-160ºC (4-6 bar) durante aproximadamente 2-4 minutos es posible hacer una pequeña extracción del contenido residual de D-limoneno en la muestra.

En este capítulo se recoge el estudio realizado a cáscara de naranja tratada mediante hidrólisis térmica con explosión de vapor bajo distintas condiciones de temperatura-tiempo.

6.2.2. Material y Métodos

La metodología seguida y el equipo empleado se han descrito previamente en el capítulo 5 de “Materiales y Métodos” (apartados 5.1.1 y 5.2.5). A continuación se recogen únicamente algunos datos concretos relativos al pre-tratamiento y los ensayos de potencial metanogénico.

a) Pre-tratamiento:

- Dispositivo experimental: La planta empleada corresponde al piloto Cambi® descrito en el apartado 5.1.1.

- Condiciones de operación: Se recogen en la tabla 6.2.2 (temperatura y tiempo). Se observa que la temperatura se estudió en el rango 170-190ºC y el tiempo se fijó en 7, 15 y 30 min. Estos valores conducen a factores de severidad (log R_0, calculados con la ecuación 5.7) en el rango 2-4.

b) Ensayos BMP

- Sustrato: cáscara de naranja.

- Inoculo: Fango mixto digerido procedente de la estación de tratamiento de aguas residuales de Valladolid con una concentración de 12 g SV/kg.

c) Caracterización inicial del residuo

La tabla 6.2.1 muestra la caracterización inicial de la muestra de cáscara de naranja empleada.

Tabla 6.2.1 – Caracterización de la muestra original de cáscara de naranja

Parámetro		Valor	Unidades
Sólidos Totales	ST	173.76 ± 1.52	g/kg
Sólidos Volátiles	SV	167.65 ± 2.33	g/kg
Porcentaje de SV	% SV	96	---
Demanda Química de Oxigeno	DQO	152.00 ± 2.34	g O_2/kg
Relación DQO/SV	DQO/SV	0.91	---

Observación: Para todos los experimentos realizados, se ha reducido el tamaño de partícula entre 3-5 cm antes del pre-tratamiento.

d) Planteamiento experimental

La tabla 6.2.2 muestra las cinco combinaciones de temperatura-tiempo ensayadas.

e) Parámetros de respuesta

Como parámetros de respuesta al pre-tratamiento, se han utilizado el factor de severidad y el factor de biodegradabilidad descritos previamente en el capítulo 5 de “Materiales y Métodos” como ecuaciones 5.7 y 5.8.

Factor de Severidad (log R_0)

$$\log R_0 = \log\left(t.exp\left(\frac{T-100}{14.75}\right)\right) \qquad (5.7)$$

Factor de Biodegradabilidad (FB)

$$FB = \frac{\left(mL\,CH_4/gSV_{añadido}\right)_{Hidrolizado}}{\left(mL\,CH_4/gSV_{añadido}\right)_{No-Hidrolizado}} \qquad (5.8)$$

6.2.3. Resultados y Discusión

La tabla 6.2.2 muestra para las cinco combinaciones temperatura-tiempo ensayadas (TH1-TH5) los resultados obtenidos tanto de productividad (calculados según descrito en el apartado 5.3) como en factor de biodegradabilidad (FB descrito en la ecuación 5.8). Dicho factor ha sido calculado con respecto al correspondiente a cáscara de naranja no tratada térmicamente (TH0).

Tabla 6.2.2 – Condiciones de pre-tratamiento y parámetros de respuesta

THi	T (ºC)	t (min)	log R_0	mL CH_4/g SV (30 días)	FB (30 días)
TH0	No tratado		0.00	236.3 ± 8	1.00
TH1	170	7	2.91	214.4 ± 7	0.91
TH2		15	3.24	187.9 ± 6	0.80
TH3		30	3.54	159.3 ± 5	0.67
TH4	190	15	3.83	145.5 ± 8	0.62
TH5		30	4.13	16.1 ± 5	0.07

La figura 6.2.1 presenta la evolución de los ensayos BMP

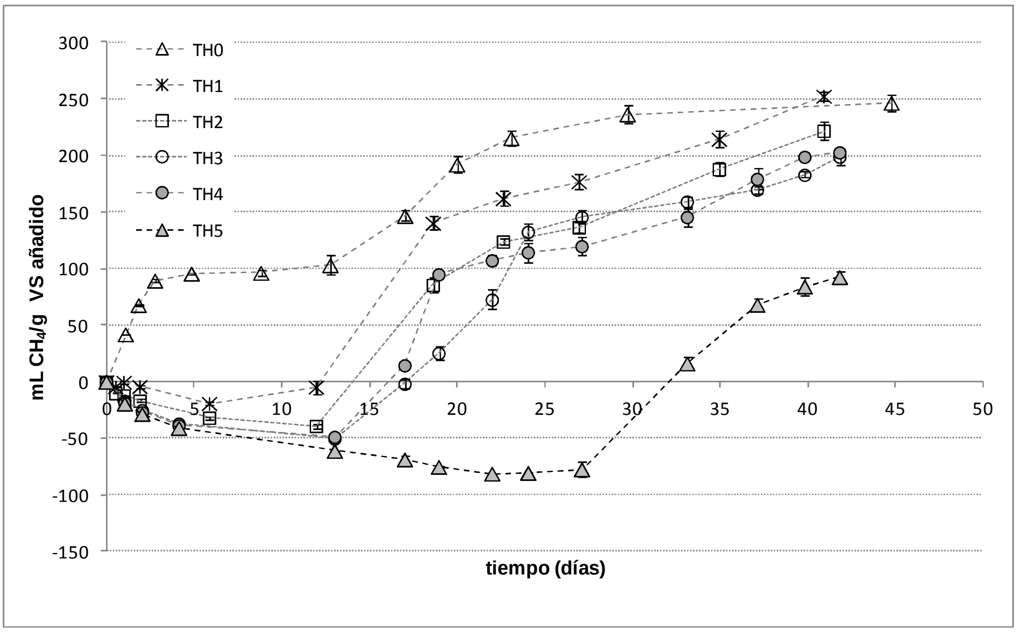

Figura 6.2.1 – Productividad en metano (mL CH_4/g $SV_{añadido}$)

La primera conclusión clara que se deduce es que el tratamiento de hidrólisis térmica a las temperaturas ensayadas de 170 y 190ºC empeora la biodegradabilidad de la cáscara de naranja, tanto en el valor final de productividad, como en cinética. De hecho, durante los primeros días de ensayo la producción de los test con sustrato pre-tratado fue inferior a la del inóculo, y por ello las productividades son negativas durante el periodo inicial de test. Este empeoramiento resulta mayor cuanto mayor es la severidad del pre-tratamiento, como muestra la figura 6.2.2.

Si bien no se han realizado analíticas específicas, la explicación de este comportamiento se encuentra probablemente en la formación de compuestos inhibitorios o recalcitrantes en el pre-tratamiento, o bien en la liberación de otros compuestos, como el D-limoneno, que inhiben las bacterias anaerobias.

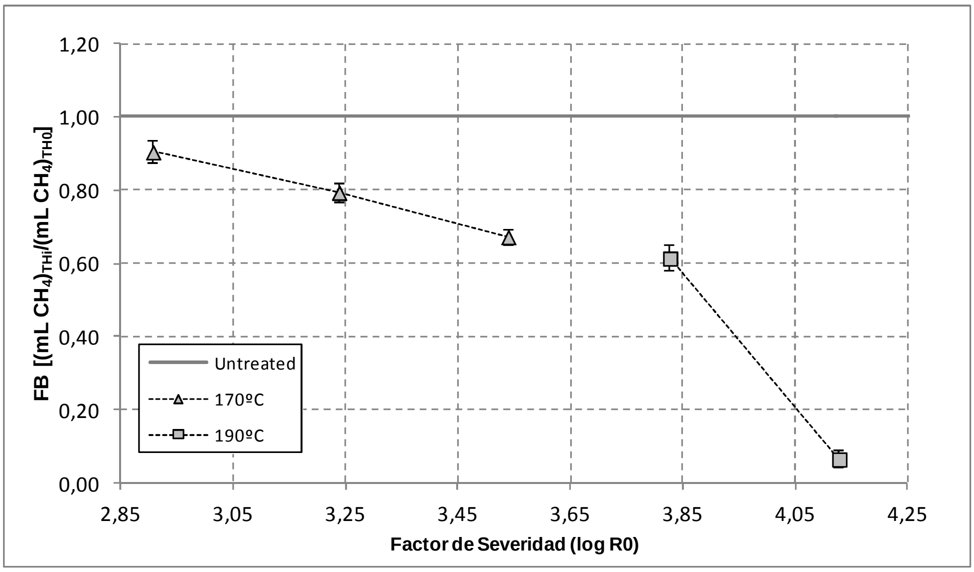

Figura 6.2.2 – Relación Factor de biodegradabilidad (FB) con el factor de severidad (log R_0) en el pre-tratamiento de hidrólisis aplicado

6.2.4. Conclusión

El pre-tratamiento de hidrólisis térmica a 170-190ºC empeora la digestión anaerobia del residuo cáscara de naranja, siendo mayor dicho empeoramiento cuanto mayor es la severidad del tratamiento (temperatura-tiempo).

Este empeoramiento es posiblemente debido a la formación de compuestos inhibitorios o recalcitrantes, o a la liberación de D-limoneno en el medio, reconocido agente antimicrobiano inhibidor de las bacterias anaerobias.

Podría resultar de interés el estudio de la influencia del pre-tratamiento en condiciones de menor severidad, pero no se ha realizado.

Finalmente, una caracterización con mayor detalle de las muestras antes y tras el tratamiento mostraría qué sustancias inhibidoras se han formado o liberado.

6.2.5. Referencias

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Apartado 6.3

Hidrólisis térmica de paja de trigo

Apartado 6.3.1

Optimización de las condiciones de operación: *"Influence of Thermal Pretreatment on the Biochemical Methane Potential of Wheat Straw."*

Apartado 6.3.1

Este apartado se describe en el artículo que sigue, correspondiente a una publicación en la revista *“Bioresource Technology”.*

“Ferreira, L.C., Donoso-Bravo, A., Nilsen, P.J., Fdz-Polanco, F., Pérez-Elvira, S.I., 2013. Influence of thermal pretreatment on biomethane potential of wheat straw. Bioresource Technology. 143, 251-257.”

A continuación se recoge dicho artículo, incluyéndose una copia de la publicación en el capítulo de “Anexos”.

Influence of Thermal Pretreatment on the Biochemical Methane Potential of Wheat Straw

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Abstract

The biochemical methane potential of steam exploded wheat straw was evaluated in a pilot plant under different temperature-time combinations. The optimum was obtained for 1min and 220ºC thermal pretreatment (3.5 severity factor), resulting in a 20% increase in methane production respect non-treated straw. For more severe treatments the biodegradability decreased due to a possible formation of inhibitory compounds. The results of the tests were modeled with a first order equation to estimate the hydrolysis constant and biodegradability extent, and the influence of temperature and time on the kinetic parameters was obtained with a response surface study. The data processing confirmed the accuracy of the model and the optimum operation conditions, and demonstrated that the biomethanization of raw and pretreated wheat straw is limited by the hydrolysis, being the individual influence of temperature and time much more important than the interaction between them.

Keywords: biochemical methane potential, thermal hydrolysis, pre-treatment, mathematical modeling, wheat straw

1. Introduction

In many countries, lignocellulosic materials are an abundant agricultural residue which can be used either for animal feeding or for energetic valorization in power plants. In Europe, wheat straw represents the largest agricultural waste, being in Spain an important part of the crop wastes which could be used as biomass for renewable energy production. The use of renewable energy sources is becoming increasingly necessary in order to cope with the impacts of global warming. The conversion of biomass into energy can be achieved in a number of ways, being anaerobic digestion a very sustainable alternative.

Anaerobic digestion is a well-known process for the treatment of wastewater of organic wastes. This process presents advantages over some conventional aerobic technologies, such as the better handling of wet waste, the production of biogas as a renewable source of energy and the attenuation of odor problems (Palmowski and Muller, 2000; Pérez-Elvira et al., 2011; Pérez-Elvira et al., 2010). Furthermore, anaerobic digestion is the most cost-effective treatment, due to high energy recovery and low environmental impact (Mata-Alvarez et al., 2000). However, the application of anaerobic digestion with lignocellulosic biomass has not been a subject of enough research.

Lignocellulosic material is mainly composed of three different types of polymers: cellulose, hemicellulose and lignin. While cellulose has a rigid and crystalline form, hemicellulose has a lower molecular weight and short lateral chains, which corresponds to an easy hydrolysable polymer. The third compound, lignin, is one of the most abundant polymers in nature. It is a complex and amorphous heteropolymer consisting of three different phenylpropane units, and is also non-water soluble (Hendriks and Zeeman, 2009). Wheat straw consists mainly of cellulose (30-40%), hemicellulose (20-30%) and lignin (10-20%).

The cellulose and hemicellulose fractions can be enzymatically hydrolyzed to monomeric sugars after a pre-treatment aiming to hydrolyze its partially crystalline structure (Puls and Schuseil, 1993).

The hydrolysis of this type of biomass is limited by several factors, such as the lignin content. In cellulose the molecules are linear, and therefore they can form hydrogen bonds between the chains that limit their solubility in water, and reduce the available surface area, making cellulose difficult to degrade. A number of pretreatments for ligmocellulosic biomass are currently available, such as mechanical, milling into smaller pieces (Mshandete et al., 2006; Palmowski and Muller, 2000), physico-chemical such as dilute alkaline pretreatment (McIntosh and Vancov, 2011) or dilute acid pretreatment (Schell and el., 2003), wet oxidation, thermal treatment (Sapci, 2013), or a combination of them (Linde et al., 2008; Nkemka and Murto, 2013). From the point of view of its applicability, the total energy balance of the global process (considering both pre-treatment and digestion) must be taken into consideration. Compared to other pretreatment methods, the thermal hydrolysis can be cost effective if a proper steam-explosion and energy recovery is performed. The warranty that the process is energetically self-sufficient is described in Pérez-Elvira and Fdz-Polanco (2012). Furthermore, hydrothermal treatment can be performed without addition of chemicals or oxygen, representing a potential solution for the pretreatment of large quantities of lignocellulosic biomass including woods material (Horn et al., 2011a; Sipos et al., 2010) and agricultural by-products (Horn et al., 2011b; Ohgren et al., 2006).

Thermal pretreatment is a method where the substrates are subjected to heating under a specific pressure during a certain period of time. At the end of the heating, a steam explosion occurs, where the biomass is rapidly discharged into normal pressure causing an explosion of the macromolecules. At temperatures in the range 150-180ºC, parts of lignocellulosic materials will start to solubilize (Garrote et al., 1999). Some studies have shown that the effect of the thermal treatment depends on several factors, such as: residence time, operating temperature, chip size, and moisture content (Bauer et al., 2009; Han et al., 2010; Zhang et al., 2008). A too harsh treatment of lignocellulosic biomass may result in a lower methane yield and longer retention time. The reason is that when lignin is broken, there is a risk of formation phenolic and hererocyclic compounds from hemicellulose and cellulose degradation, like furfural and hydroxymethylfurfural (HMF), which are known to inhibit many fermented microorganisms, including those involved in the biogas generation (Hendriks and Zeeman, 2009). According to Raj (2009) the concentration of furfural that inhibits methanogens ranges from 2,400 to 3,000 mg/L.

The aim of this research is to study the impact of thermal hydrolysis on the biodegradability of wheat straw under mesophilic anaerobic conditions, by using an experimental approach and mathematical modeling of the results. The final applicable objective is to define the pretreatment parameters that optimize the methane productivity.

2. Materials and Methods

2.1 Raw Material

Wheat straw was grown in Valladolid (Spain) and harvested in 2011. For all the experiments, the straw was cut into pieces of 10 cm long. The average values obtained in wheat straw characterization are: 922±2 g TS/kg (92%VS/TS), 1078±8 g TCOD/kg, 4.72 g N-TKN/kg, and a ratio C/N around 92.

2.2 Thermal Pre-Treatment pilot plant and operation conditions

The Cambi® thermal treatment plant, steam explosion unit, consists of a 30 L reactor and a flash tank with a removable bucket to collect the pretreated material (Fig. 6.3.1.1). The steam is generated by a 25 kW electric steam boiler (200 L capacity) which can supply steam up to a maximum pressure of 34 bar (240ºC). Wheat straw is loaded into de reactor using a motorized (M) ball valve (V4) at the top of the reactor. Steam is added to the reactor from the bottom, through an air-actuated valve (V1), heating the waste during the time established. The desired operation pressure (corresponding to a certain temperature) is set on the control panel unit, controlled automatically by the air-actuated valve (V1). For security reasons also a manual valve (V2) has to be opened to add steam to the pressure reactor. An air-actuated ball valve at the bottom of the vessel (V3) is responsible for the rapid pressure drop (explosion) and release of the pretreated biomass to the flash tank. The pretreated biomass is collected in a removable bucket at the bottom of the flash tank. The steam that is leaving the flash tank is condensed and led to a water tank (WT). Any steam that is not condensed leaves the unit via a carbon filter (CF) to remove smell.

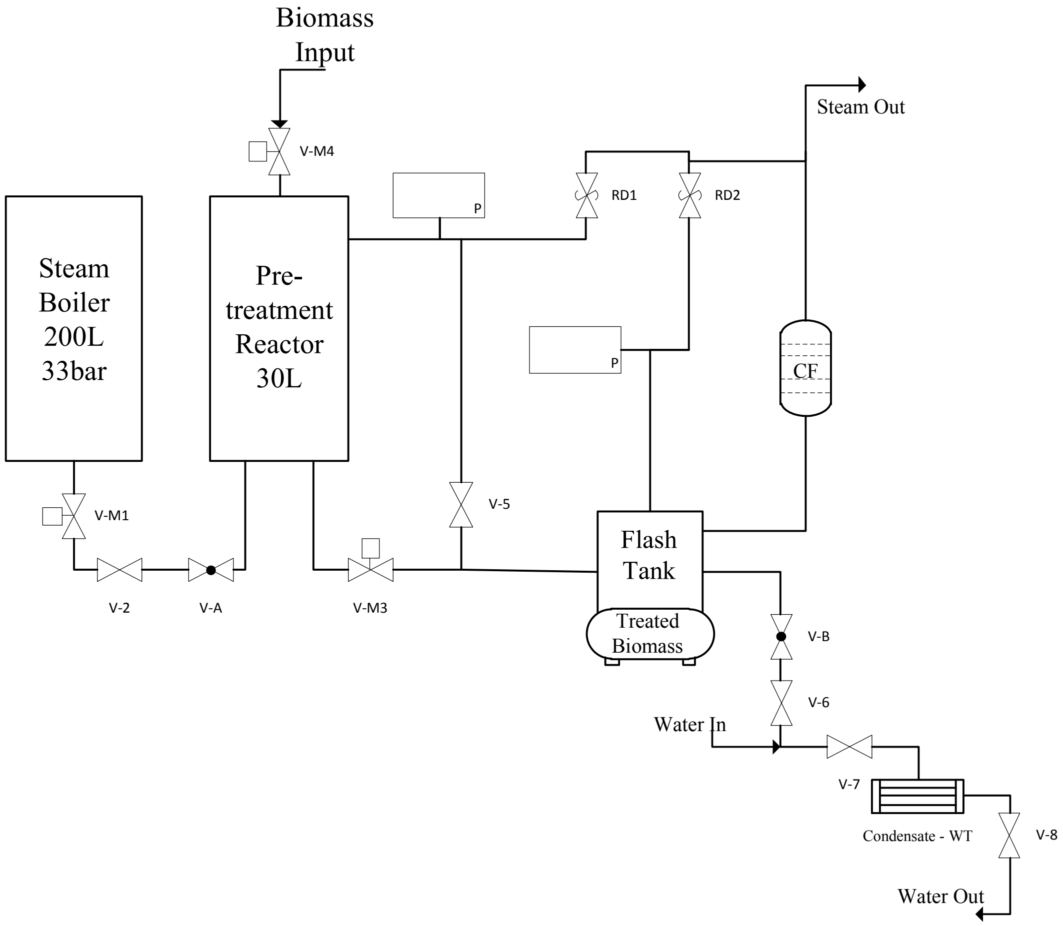

Figure 6.3.1.1. Cambi® steam explosion unit. V - valves; VM - motorized valves; VA,B – one way valves; P – manometers to measure pressure; RD – safety valves; CF – carbon filter; TB-T – treated biomass tank; WT – Water tank

Different pre-treatment conditions were tested varying both temperature (ranging 150-220°C) and time (ranging 1-15 minutes). In all the experiments, one kilogram of wheat straw was used. The reactor was preheated for about 15 min at the same temperature selected for the pre-treatment before starting the experiments.

Temperature and time determine the severity factor of the treatment. This parameter (log R_0, eq. 6.3.1.1) is most widely accepted for steam pre-treatments (Hendriks and Zeeman, 2009) to express the severity of the pre-treatment:

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \qquad (6.3.1.1)$$

where *t* is the time (min), *T* the temperature (°C), *100* is the base temperature (100ºC), and *14.75* is the activation energy based on the assumption that the reaction is hydrolytic and the overall conversion is first order (Xu et al., 2011). This expression only takes into account time and temperature, and does not consider the effect of the flash. The study of this effect is not assessed in this paper.

Theoretically, the more severe a treatment is, the more cellulose is made available for digestion. However, very severe pre-treatments can lead to formation of inhibitory compounds from the macromolecules, driving to an indirect relationship between the severity factor and the biodegradability. Therefore there should be an optimum value for the severity factor.

2.3 Anaerobic Biodegradability

Batch anaerobic digestion tests (BMP) were carried out in triplicate to assess the wheat straw biodegradability after the different pre-treatment conditions applied. A control test without substrate and a control with cellulose were included in order to check the methanogenic activity of the inoculum. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1±0.3ºC), with constant mixing in a rotary desk

The anaerobic inoculum used for the batch test was taken from a pilot-scale mesophilic anaerobic digester treating mixed sludge from a municipal wastewater treatment plant, with a volatile solids (VS) concentration of 12 gVS/kg. The inoculum was pre-incubated for four days (35.1±0.3ºC) in order to minimize its residual biodegradable organic material content.

Bottles of 2L volume were used, made of borosilicate glass (260 mm height, 160 mm diameter and a 40 mm bottleneck), placed horizontally in a rotary table to achieve a good mixing. The liquid volume was 400 mL in order to have enough headspace, and the substrate/inoculum (S/I) ratio selected was 0.5gVS/gVS as suggested by Neves et al., 2004 and Angelidaki et al., 2009.

Biogas production was measured manually by a pressure transmitter (ifm, PN5007, range 1 bar) in the head space of each reactor and the biogas composition was measured by gas chromatography (Varian CP-3800 CG TCD). The biogas production was followed for about 40 days. All values of specific methane yield (mL CH_4/ gVS_{fed}) are presented under standard temperature and pressure conditions (STP – 0ºC, 1 atm) defined by IUPAC (International Union of Pure Applied Chemistry), and divided by the mass of volatile solids of substrate fed into the assay.

Theoretical methane yield (Nm^3 CH_4/kg VS) was calculated from the characterization performed to the wheat straw as follows:

$$350 \text{ mL } CH_4/\text{g } TCOD_{removed} \times 1.27 \text{ g TCOD/g VS} = 444 \text{ mL } CH_4/\text{g } VS_{removed}$$

This value is in agreement with the one calculated by Kaparaju et al. (2009) considering the stoichiometric conversion of the organic matter (426 mL CH_4/g $VS_{removed}$).

2.4 Analytical Method

Substrates, inoculum and digestates were characterized in all the experiments. Total and volatile solids (TS and VS) and total Kjeldahl nitrogen (TKN) were measured following the procedures given in Standard Methods for Examination of Water and Wastewater (APHA et al., 2005). Total chemical oxygen demand (TCOD) was determined according to standard UNE 77004:2002 based in dichromate method. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

2.5 Parameters determination and evaluation methodology

2.5.1 Parameters determination from BMP test

When the hydrolysis reaction is the rate-limiting step of the global process, as happens in the anaerobic degradation of lignocellulosic substrates, the first order model (equation 6.3.1.2) is commonly used to estimate the reaction extent B_0 (related to the substrate biodegradability) and the hydrolysis constant k_h ,which both could be used in a global model of the anaerobic digestion process (such as ADM1) to predict the performance of the anaerobic digester (Batstone et al., 2009; Donoso-Bravo et al., 2010; Ge et al., 2011).

$$B = B_0 \cdot (1 - \exp(-k_h \cdot t)) \qquad (6.3.1.2)$$

where B is the biogas production (ml/gVS$_{\mathrm{fed}}$)

2.5.2 Model accuracy determination

Apart from obtaining the best combination of parameters, it is even more important to know the accuracy of the estimated values. The Fisher matrix (FIM) summarizes the quantity and quality of the information obtained in the experiment and, assuming proper model selection with no data autocorrelation and uncorrelated error, the inverse of the FIM (equation 6.3.1.3) corresponds to the parameter estimation covariance matrix (C_j)

$$C_J = (F(\theta))^{-1} \qquad \text{where} \quad F(\theta) = \sum_{i=1}^{N} \left[\frac{\partial y_i(t,\theta)}{\partial \theta} \right]^T Q_i^{-1} \left[\frac{\partial y_i(t,\theta)}{\partial \theta} \right] \qquad (6.3.1.3)$$

Finally, once the covariance matrix is available, an approximation of the standard deviation of the parameters can be estimated through equation (6.3.1.4).

$$\sigma(\theta_i) = \sqrt{C_J} \qquad (6.3.1.4)$$

2.5.3 Response surface methodology (RSM)

This methodology allows evaluating the combined effect of several variables (temperature and time in this case) and the interaction between them on a specific response (in this case, those parameters obtained in sub-section 2.5.2). The polynomial shown in equation (6.3.1.5) considers the effect of both variables as well as the combined influence of them. The coefficients of the equation were obtained by minimizing the least square function, and determination coefficient was calculated to know the fraction of the variability of the data that is explained by the model. The analysis was carried out in Matlab®.

$$Y = p_1 + p_2 x_1 + p_3 x_2 + p_4 x_1 x_2 \tag{6.3.1.5}$$

where Y is the variable response, x_1 is the pretreatment time, x_2 is the pretreatment temperature, and $p_1 ... p_4$ are the regression coefficients of the model.

3. Results and Discussion

3.1 Pre-treatment experimental study

The temperature-time combinations selected for the study are presented in Table 6.3.1.1. For each experiment the severity factor (log R_0) was calculated according to equation (6.3.1.1). The last column in Table 6.3.1.1 presents the results for the normalized production on methane (FN) defined as the ratio between the production of methane for the treated and untreated wheat straw: $(\text{mL CH}_4)_{\text{THi}}/(\text{mL CH}_4)_{\text{untreated}}$.

Table 6.3.1.1. Conditions applied for the different experiments performed

Experiments	Ref.	P (bar)	T (ºC)	time (min)	log R_0	mLCH_4/g VS_{fed}	FN
Untreated	0	---	---	---	---	226±11	---
TH-1	1	5	150	15	2.65	185±28	0.82
TH-2	2	8	170	5	2.76	159±16	0.70
TH-3	3	8	170	15	3.24	250±19	1.10
TH-4	4	16	200	2	3.25	211±22	0.93
TH-5	5	16	200	5	3.64	238±18	1.05
TH-6	6	16	200	15	4.12	202±2	0.89
TH-7	7	23	220	1	3.53	273±3	1.21
TH-8	8	23	220	5	4.23	214±28	0.95

Compared to the theoretical methane productivity (444 mL CH_4/g $VS_{removed}$), the experimental value obtained in the BMP test of the untreated wheat straw indicates that only 51% of the volatile solids were converted into methane. For the best thermal hydrolysis conditions (TH-7) the anaerobic biodegradability increased until a value of 61%.

Figure 6.3.1.2 shows the relation between the severity factor and the normalized production of methane. The influence of the severity factor is quite clear: when increasing the severity factor, the production of methane increases until reaching a maximum. Over this optimum, the efficiency of the pretreatment decreases and therefore the methane production does, probably due to the formation of inhibitory compounds. For example, Thomsen et al (2009) obtained an increase in the furfural concentration from 50mg/L to 1,200mg/L when increasing the pretreatment temperature from 190ºC to 205ºC (6 minutes treatment).

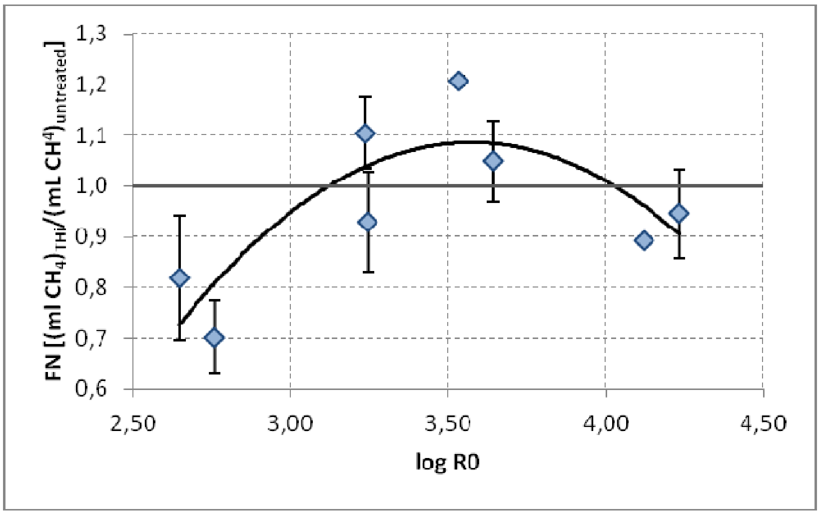

Fig. 6.3.1.2 – Normalized methane productivity (FN [(mL CH_4)$_{THi}$/(mL CH_4)$_{untreated}$]) with respect to the severity factor (log R_0)

In the present study, the highest improvement with respect to the untreated sample corresponds to the severity factor in the range 3.25-3.5.

Further analysis of the results is necessary in order to determine the best way of coupling temperature and time to get a desired severity factor (that is: short pre-treatment at high temperature, or the contrary). Therefore, subsequent modeling and RSM evaluation was performed.

3.2 Modeling of the results and parameters determination

Fig. 6.3.1.3 presents the fitting process between the experimental methane production and the first order model curve. It can be observed that the model is able to reproduce the methane production profiles in a proper way since in most of the cases the model curve lies inside the corridor given by the standard deviation (SD). Moreover, the determination coefficients (R^2) are mostly above 0.98, which indicates that this model is able to explain around 98% of the experimental data variability. Table 6.3.1.2 shows the values obtained in the parameters estimation where it can be observed that the standard deviation of the estimated parameters was not significant with respect to the mean values, hardly over 10% compared to the optimized values, which is also an indicator of the model fitting procedure success.

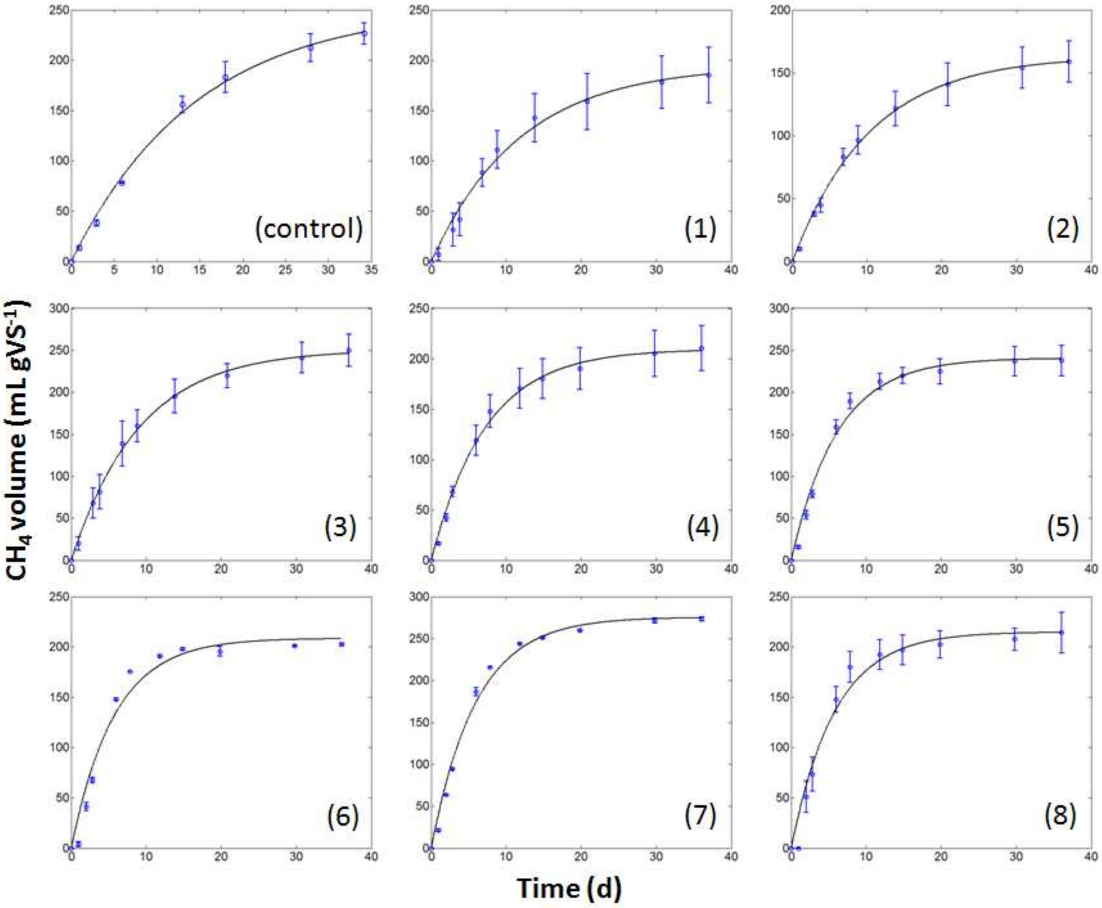

Fig. 6.3.1.3 First order model fit. Experimental information (blue points), model profile (black solid line)

Table 6.3.1.2. Results of the parameters determination

			First order Model				
	T	**t**	B_0		k_h		R^2
Exp.	**(°C)**	**(min)**	**mean**	**SD***	**mean**	**SD***	
0	0	0	252.1	9.2	0.069	0.006	0.997
1	150	15	194.6	8.2	0.085	0.009	0.989
2	170	5	163.4	3.0	0.097	0.005	0.997
3	170	15	250.6	3.6	0.110	0.004	0.998
4	200	2	209.2	4.0	0.138	0.008	0.995
5	200	5	240.7	6.8	0.164	0.015	0.987
6	200	15	208.6	9.3	0.175	0.025	0.968
7	220	1	275.5	6.9	0.168	0.014	0.989
8	220	5	214.9	8.7	0.173	0.023	0.973

***SD**: Standard deviation

With respect to the values of the parameters, the first order model fit shows that the thermal pretreatment had a positive influence on the hydrolysis rate (Fig. 6.3.1.3): this means that the higher the severity factor, the higher the hydrolysis constant. These results show that the solubilisation of particulate organic matter is a consequence of both temperature and time effects. Although the solubilized biomass is expected to be more available for the anaerobic biomass, the results show that in some cases the pretreatment lead to a decrease in biodegradability, especially for the highest severity factors. This can be explained due to the appearance of some recalcitrant compounds after the pretreatment, as aforementioned.

3.3 Response surface methodology (RSM) results

The parameters of the first order model were fitted to a polynomial equation to evaluate the influence of the two independent variables (temperature and time). The obtained equations are shown next:

$$k_H = 0.152 - 0.003 \cdot T + 0.0014 \cdot t + 0.000027 \cdot T \cdot t \qquad (6.3.1.6)$$

$$B_0 = -249.48 + 31.58 \cdot T + 2.33 \cdot t - 0.1582 \cdot T \cdot t \qquad (6.3.1.7)$$

In the operation range evaluated, the influence of the interactions between both parameters is low compared to the independent influence of each one. In the case of k_H, the determination coefficient (R^2) was 0.958, which means that the model correlates around 96% of the variability in the parameter. Therefore, this empirical model can be used to predict the hydrolysis constant using the data of temperature and pretreatment time within the studied design range. For B_0, the determination coefficient was not as good as expected (0.569), which may indicate that this type of polynomial model may not be the best option to predict this parameter. The results of the agreement between the k_H and B_0 values obtained from the BMP test and the predicted ones with the polynomial are presented in Fig. 6.3.1.4. Globally, there is a good agreement between the predicted and the actual values of the parameter, especially in the case of the hydrolysis constant.

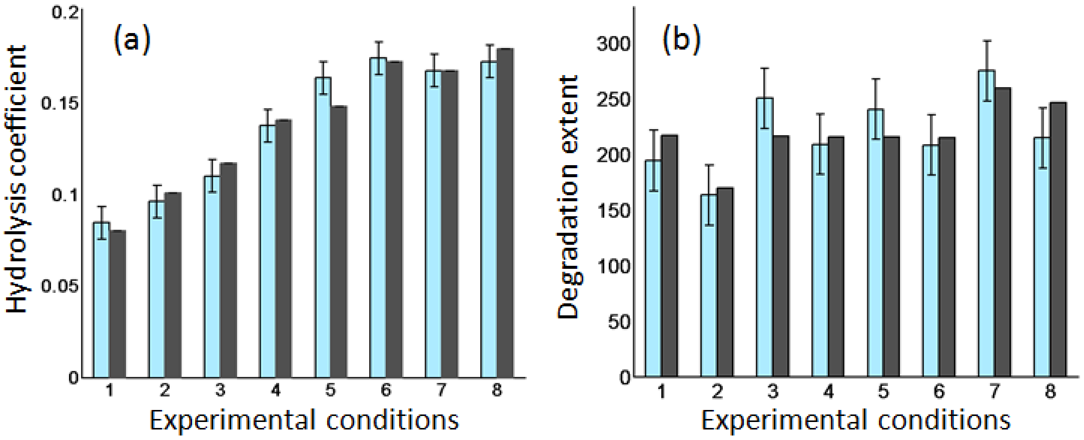

Fig. 6.3.1.4 Comparison between model prediction and the experimental data by using the optimal set of parameter values. (a) Hydrolytic coefficient (b) degradation extent. Light blue bars: real values, grey bars: predicted by the polynomial

By applying these polynomial equations, two surface responses were built in order to observe optimum region of the parameters in terms of temperature and time (Figure 6.3.1.5). In the case of k_H, the optimum zone (red zone) can be observed toward the higher values of both temperature and time, which must entail that the soluble fraction of the organic matter increases when increasing these variables. By contrast for B_0, the best values were obtained at higher temperatures and short times. Therefore, the conclusion about the best way of coupling temperature and time to get the optimum severity factor around 3.5 is: high temperature (220ºC) and short time (1 min), instead of the contrary (lower temperature but higher time).

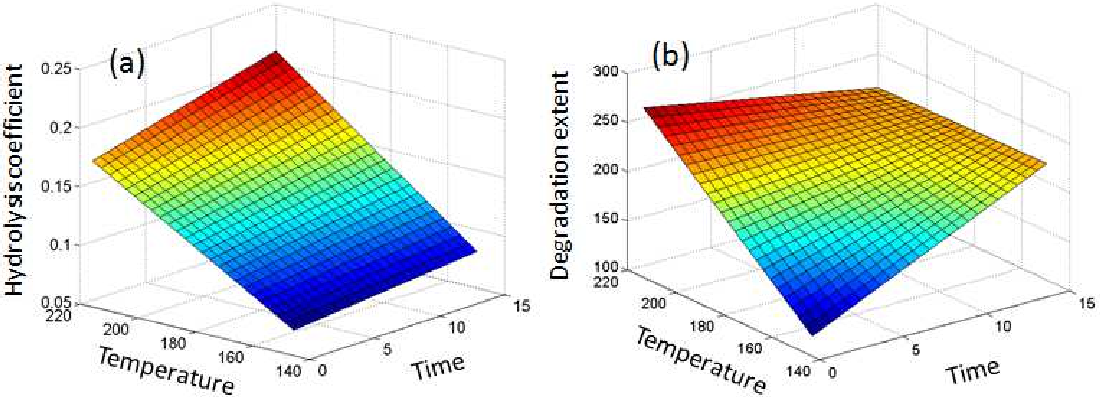

Fig. 6.3.1.5 Response surface graphs (a) Hydrolytic coefficient (b) degradation extent

4. Conclusions

The influence of thermal pretreatment parameters (temperature and time) on the anaerobic biodegradation of wheat straw was evaluated. In terms of “severity factor”, the optimum was obtained at 3.5, corresponding to 220ºC and 1 min treatment. A first order model fitted accurately the experimental results on biodegradability, confirming that the hydrolysis is the limiting step. A surface response methodology was applied to assess the combined effect of the temperature and the time on the kinetic parameters, which indicated that influence of the interactions between these variables is low in comparison with the separated influence of each one.

Acknowledgments

This work was financially supported by the company Cambi®, project “Thermal hydrolysis of solid wastes”. The group of Valladolid University is *Grupo de Excelencia GR 76 de la Junta de Castilla y León* and member of the Consolider- Novedar framework (Programa Ingenio 2010). A. Donoso-Bravo is supported by the “Dirección de Investigación (DII)” of the Pontificia Universidad Católica de Valparaíso

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Apartado 6.3.2

Estudio de otros parámetros de operación

“Biomethane Potential of Wheat Straw – Influence of particle size, water impregnation and thermal hydrolysis.”

Apartado 6.3.2

Este apartado se describe en el artículo que sigue, correspondiente a una publicación en la revista “*Chemical Engineering Journal*”.

A continuación se recoge dicho artículo, incluyéndose una copia de la publicación en el capítulo de “Anexos”.

Biomethane potential of wheat straw: influence of particle size, water impregnation and thermal hydrolysis

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Abstract

The anaerobic digestion of organic wastes such as wheat straw represents a very interesting means of generating biogas while reducing the amount of waste to disposal. An enhancement in the hydrolysis limited digestion of straw can be achieved by optimizing operation and performing pre-treatments. In this study, the influence of particle size, water impregnation and thermal pre-treatment was investigated through biochemical methane potential tests (BMP). The maximum methane yield was obtained by heating the straw at 200ºC for 5 min followed by steam explosion, obtaining a 27% increase in methane productivity compared to non-treated straw (from 233 to 296 mL CH_4/gVS_{fed}). Cutting (3-5 cm) showed to be better than milling (<1 mm), and the impregnation of the straw with water helped to enhance BMP test results by 4-10% (supposed better mixing due to a 10 times reduction of solids concentration) but had no effect on thermal pre-treatment. On the contrary, the economic impact of milling and water addition on a thermal pre-treatment would be absolutely negative, increasing the operation cost necessary to reduce the size and to heat water, respectively.

Keywords: biochemical methane potential (BMP), particle size, thermal hydrolysis pre-treatment, wheat straw

1. Introduction

Wheat straw is the largest agricultural residue in Europe, and the second largest in the world, after rice straw [1, 2]. Nowadays straw is either used as bedding material for livestock, applied to the soil as natural fertilizer or as biomass for energetic valorization. The search for renewable energy sources together with the concern on greenhouse gas emissions have increased the interest on lignocellulosic materials as a source of energy [3, 4], which is particularly well suited for energy applications because of its large-scale availability, low cost and large production.

Anaerobic digestion of biomass is a more economical and environmentally beneficial way of biomass utilization compared to typical pathways to biodiesel or bioethanol [5].

However, the main obstacle impeding a more widespread application of straw as feedstock for anaerobic digestion is its low digestibility due to its refractory structure. Like other lignocellulosic biomass, wheat straw is a complex mixture of cellulose, hemicellulose and lignin. Bioconversion of wheat straw is favored because of its relatively low lignin content (15-20%) and high carbohydrate content (30-40 and 20-30 %w/w cellulose and hemicellulose, respectively) [6]. Lignin surrounds and seals the cellulose structure while hemicellulose serves as a connection between both of them [7]. Therefore, hydrolysis is a slow and difficult process [8, 9].

In order to improve the biodegradability of wheat straw, several methods have been investigated, such as mechanical size reduction from the organic particulate matter [10, 11, 12, 13], or the introduction of a lysis pre-treatment, such as physico-chemical alkaline dilution [14], microwave pre-treatment [15, 16] or thermal steam explosion [17, 18, 19]. This last option has proven to be very interesting, as it can be cost effective if a proper energy recovery is performed. Hydrothermal steam explosion is performed without the addition of chemicals or oxygen, representing a potential solution for the pre-treatment of large quantities of lignocellulosic biomass [1; 20].

In a steam explosion, biomass is heated and rapidly discharged to atmospheric pressure causing the explosion of the macromolecules, with the aim of upgrading the digestibility of lignocellulosic materials, by increasing porosity, removing lignin content and promote hemicellulose hydrolysis [18, 21]. Although the successful use of steam explosion has been proved from the point of view of fermentation and ethanol production [1, 22, 23, 24, 25], the evaluation of the methane potential of steam-exploded straw is more recent [19, 21, 26], and open to many other wastes (corn stover, maizecrop waste, rice straw, herbaceous waste, manure, sewage sludge).

The studies performed specifically with wheat straw [1, 18, 21] have shown that the effect of the thermal pre-treatment depends on several factors, such as chip size, temperature and time. It is generally accepted that there is an optimum temperature in the range of 150-220ºC and 5-20 minutes, but care must be paid for too severe treatments due to the formation of inhibiting phenolic and heterocyclic compounds, such as furfural [10].

Chip size is a crucial parameter, as any sort of cutting or milling is necessary to avoid clogging and heat transfer problems during thermal treatment (overcooking the outside of large chips and formation of inhibitory compounds). However, a promising finding is that enzymatic hydrolysis is improved for larger biomass particle sizes [27], as milling is an energy intensive and expensive process. Regarding the anaerobic digestion process, the effect of particle size reduction on methane yield of agricultural wastes is contradictory: positive in some studies [12, 28, 29], while negative in others [30, 31]. Therefore, the influence of particle size on wheat straw digestibility is still open to research.

The effect of water impregnation on thermal hydrolysis is a novel study in this paper. The impregnation of straw with acid or alkali has been successfully applied in enzymatic hydrolysis, while the influence of humidity on steam explosion effect is unexplored from the point of view of later methanization. From another point of view, dilution can be imperative to avoid overload or inhibition during the anaerobic digestion [32].

The aim of the present study is to evaluate the effect of particle size, dilution and thermal pre-treatment variables (temperature, time and water impregnation) on the biodegradability of wheat straw. For this purpose, batch anaerobic biodegradability tests were performed in order to check the biochemical methane potential (BMP) under different milling, washing and thermal hydrolysis conditions to determine individual and combined effects. Furthermore, a kinetic model has been used to obtain the specific rate constants to assess the relationship of the parameters evaluated.

2. Materials and Methods

2.1 Raw Material and experimental set-up

Wheat straw was grown in Valladolid (Spain), harvested in 2012 and characterized (Table 6.3.2.1). The original straw was ground (3-5 cm) or milled (<1 mm), according to the experimental set-up in Table 6.3.2.2.

Table 6.3.2.1. Average characteristics of the original wheat straw

	TS (g/kg)	VS (g/kg)	TCOD (g/kg)	TKN (g N/kg)	TOC (% weigh)	C/N
Series A-B	895 ± 11	821 ± 9	1075 ± 8	4.723	43.2 ± 0.3	92
Series C	924 ± 9	846 ± 5	1089 ± 6	4.578	43.4 ± 0.2	92

Table 6.3.2.2. Experimental set-up

Series A			Series B				Series C			
Test	Particle size	Dilution	Test	T (ºC)	t (min)	log R_0	Test	T (ºC)	t (min)	Washing time (h)
A1	3-5 cm	No	B0	Untreated			C1	200	5	0
A2	3-5 cm	Yes	B1	170	15	3.2	C2			3
A3	<1mm	No	B2	200	5	3.6	C3			12
A4	<1mm	Yes	B3	220	1	3.5	C4			24

Three series of experiments (A, B and C) were performed (Table 6.3.2.2) to cover the three scenarios to study: A. Influence of particle size and water dilution on wheat straw digestibility; B. Influence of steam explosion pre-treatment; and C. Influence of water impregnation time on thermal hydrolysis and digestion.

2.2 Particle size reduction and water impregnation

Based on bibliography (where references to particle sizes ranging from 0.2 mm to 10 cm can be found), two particle sizes were selected for series A: 3-5 cm pieces and powder < 1mm. In most of the references, the particle size influence is not assessed but established in the range of 1-5cm [12, 18, 21, 33].

The larger particle size was chopped with a cramp to get the desired interval 3-5 cm. A laboratory mill (Philips, HR7775) was used to grind the straw into a minor particle size (<1 mm) controlled with a sieve (CISA™). In the studies of series B and C only the major particle size were used.

Water addition in series A and C was performed by mixing the straw with water. In series A, the water was added when preparing the BMP tests (1:10 dilution), while in series C the straw was soaked for a desired washing time.

2.3 Thermal steam explosion pre-treatment unit plant

The pre-treatment was performed at the steam explosion pilot plant facility designed by Cambi AS and located at the wastewater treatment plant of Salamanca, Spain.

The steam explosion unit consists of a 30 L reactor vessel and a flash tank with a removable bucket to collect the pretreated material (Fig. 6.3.2.1). The steam is generated by a 25 kW electric steam boiler (200 L capacity) which can supply steam up to a maximum pressure of 34 bar (240ºC). Wheat straw is loaded into the reactor using a motorized ball valve (V1) at the top of the reactor. Steam is added to the reactor from the bottom, through an air-actuated valve (V2), heating the waste during the time established. The desired operation pressure (corresponding to a certain temperature) is set on the control panel unit, controlled automatically by the air-actuated valve (V2). For security reasons also a manual valve (V3) has to be opened to add steam to the pressure reactor. An air-actuated ball valve at the bottom of the vessel (V4) is responsible for the rapid pressure drop (explosion) and release of the pretreated biomass to the flash tank. The pretreated biomass is collected in a removable bucket at the bottom of the flash tank. Any steam that is not condensed leaves the unit via a carbon filter to remove smell.

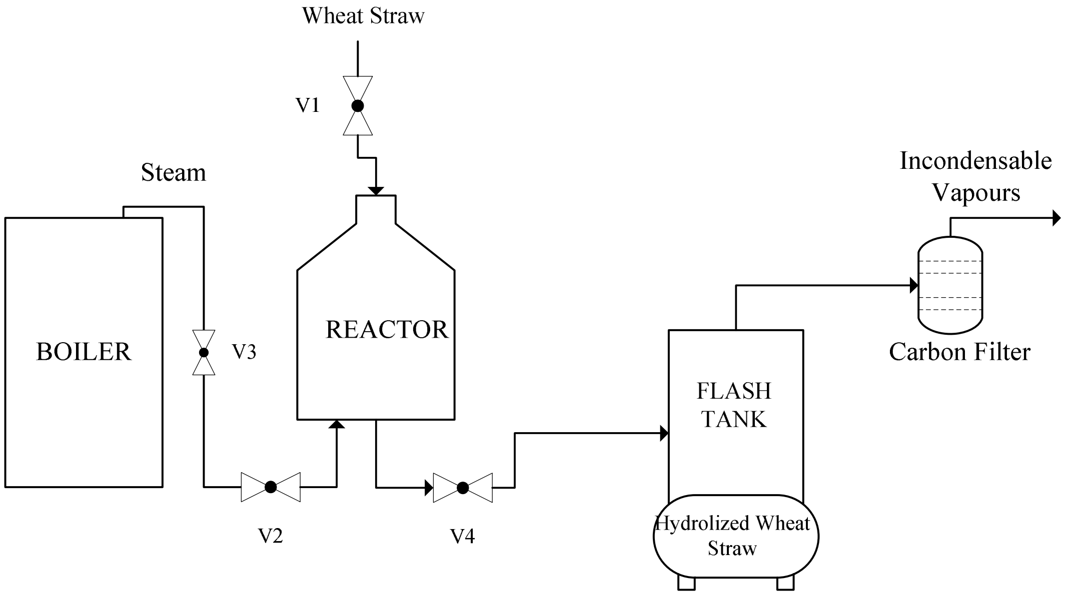

Figure 6.3.2.1 Cambi SA steam explosion unit. V - valves

In all the experiments, one kilogram of wheat straw was used. The reactor was fed to the unit and the reactor was pre-heated for 15 min before starting the experiments.

The effects of temperature and time were evaluated based on the severity factor (log R_0, Equation 6.3.2.1), which is the common term used in steam pre-treatments [11].

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \qquad \text{(Equation 6.3.2.1)}$$

where t is the time (min) and T the temperature (°C).

Different pre-treatment conditions were tested varying temperature (ranging 170-220ºC) and time (ranging 1-15 minutes), based on previous studies [14, 21, 26] concluding that the optimum severity factor (log R_0 – Equation 1) is in the range 3.3-3.6, and this criteria was considered to establish the combinations of temperature and time for series B.

2.4 Biochemical methane potential tests (BMP)

Batch anaerobic digestion tests were carried out in order to assess the wheat straw biodegradability after the different pre-treatment conditions applied. All tests were in triplicate in a 2 L borosilicate glass (260 mm height, 160 mm diameter and a 40 mm bottleneck) with 400 mL of a mixture of wheat straw and inoculum (with 12 g VS/kg and collected from a pilot digester treating waste activated sludge at 35ºC). The substrate to inoculum ratio (S/I) selected was 0.5 g VS/g VS as suggested in a previous researchers [32, 34]. A control test without substrate was included in order to check the methanogenic activity of the inoculum.

Before starting the test, the bottles were closed with ruber stoppers and aluminium crimps and degassed. Helium gas was circulated in the gas chamber for 5 minutes, and the test started after releasing the pressure. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1±0.3ºC), with constant mixing in a rotary desk. All the assays were finished when the methane production was below 5% of the total cumulative production.

The biogas volume was monitored by period measurements of the headspace pressure by a manually pressure transmitter (ifm, PN5007, range 1 bar).

The methane production of a control test performed with only inoculum was subtracted to obtain the real methane production from the straw. This value was finally expressed as specific methane yields (mL CH_4/g VS_{fed}), presented under standard temperature and pressure conditions (STP – 0ºC, 1 atm) defined by IUPAC (International Union of Pure and Applied Chemistry), and divided by the mass of volatile solids of substrate fed into to the assay.

The kinetics of methane production was calculated using a first-order model (Equation 6.3.2.2), applied successfully in other reports on anaerobic biodegradability tests [26, 35].

$$B = P.\left(1 - exp\left(\frac{-Rm\,(t-\lambda)}{P}\right)\right) \qquad \text{(Equation 6.3.2.2)}$$

Where B is the methane production (mL CH_4/gVS), P is the maximum methane production (mL CH_4/gVS), Rm is the maximum biogas production rate (mL CH_4/gVS·d), λ is the lag time (d) and t is the time of the assay (d). The data were analysed with Statgraphics® [36].

2.5 Analytical methods

Total and volatile solids (TS and VS) and total Kjeldahl nitrogen (TKN) were measured following the procedures given in Standard Methods for Examination of Water and Wastewater [37]. Total chemical oxygen demand (TCOD) was determined according to standard UNE 77004:2002 based in dichromate method [38]. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

3. Results and Discussion

3.1 Series A: Influence of particle size and dilution on wheat straw digestibility

Figure 6.3.2.2 and Table 6.3.3.3 present the results for the methane production curves (from BMP tests) and kinetic parameters for the series of tests A.

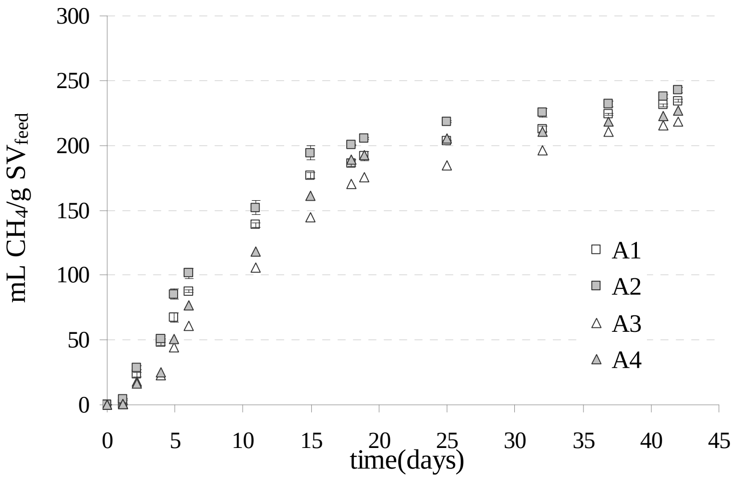

Figure 2 Methane yield for series A

Table 6.3.2.3. Results for methane yield and kinetic parameters for series A

Parameter	A1	A2	A3	A4
P (mL CH_4/gVS) [a.]	239	245	232	239
Rm (mL CH_4/gVS.d) [b.]	20.2	23.2	15.9	18.3
λ (day) [c.]	0.9	0.8	1.2	1.2
R^2	0.996	0.994	0.991	0.988

[a.] P: maximum methane production; [b.] Rm: maximum biogas production rate; [c.] λ: lag time (according to Equation 6.3.2.2)

The results show that when adding water (tests A2-A4 compared to A1-A3) methane production slightly increased (4% increase for test A2 compared to A1, at 3-5cm straw size, and 10% increase for test A4 compared to A3, at 1mm straw size), and also did the production rate (5% increase for test A2 compared to A1, and 15% increase for test A4 compared to A3). The reason is probably related with a better mixing in the BMP tests performed with water (A2 and A4), as the solids concentration in the test decreased from 200g/kg to 20 g/kg.

Analyzing the influence of the particle size by comparing tests A1-A2 with A3-A4, it can be observed that the methane production was 5-13% higher for the larger particle size, and the kinetics were also faster. These results are in agreement with those obtained by De la Rubia et al. (2011) [30] for sunflower oil cake, and Izumi et al. (2010) [31] for food waste, but disagree with the results obtained by other authors.

Sharma et al. (1988) [39] found a significant increase in methane productivity of wheat straw by size reduction from 30 mm (192 mL/gVS) to 1mm (241 mL/gVS) but only a small effect for further size reduction to 0.1 mm. Hjorth et al. (2011) [29] obtained 70% increase in methane production for extruded straw respect non-extruded straw (150 mL/gVS), although no particle size values for treated straw are given. Friction heat and shear forces in the extruder could play an important role additional pre-treatment to the cutting. Palmowski and Müller (2000) [12] obtained 57% and 86% increase in methane yield for particles of 5 cm and 0.2 cm respectively, as compared to the untreated sample (182 mL/gVS).

Putting together these results with those obtained in the present research, it can be concluded that the composition of the biowaste should be assessed to compare small and large chip sizes, as the content of carbohydrates, proteins and lipids is not uniform in the different particle size fractions but have a clear different methane potential. If no organic matter is removed during the mechanical treatment cutting seems to be better to milling or grinding in order to minimize the energy input, as milling is not considered economically feasible due to the high energy requirements,

Based on these results, wheat straw with 3-5 cm was selected to be used in series B and C.

3.2 Series B: Influence of steam explosion pre-treatment

The results of the BMP tests performed for series B and the kinetic parameters obtained are presented in Figure 6.3.2.3 and Table 6.3.2.4, where B0 corresponds to non-treated wheat straw, cut to 3-5 mm.

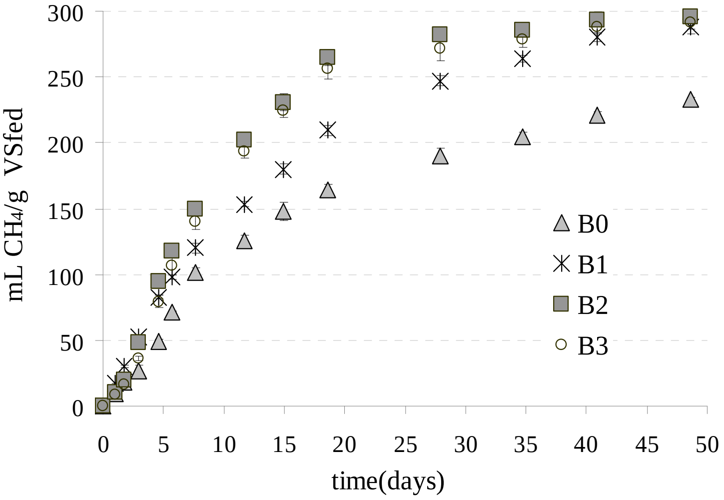

Figure 6.3.2.3. Methane yield for series B

Table 6.3.2.4. Results for methane yield and kinetic parameters for series B

Parameter	B0	B1	B2	B3
P (mL CH_4/gVS) [a.]	245	291	304	301
Rm (mL CH_4/gVS.d) [b.]	16.1	20.6	28.5	26.2
λ (day) [c.]	0.8	0.4	0.9	1
R^2	0.985	0.997	0.995	0.991

[a.] P: maximum methane production; [b.] Rm: maximum biogas production rate; [c.] λ: lag time (according to Equation 6.3.2.2)

In all steam-explosion experiments (B1-B3), the methane yield was higher than B0 (233 mL/dVS) in the range of 24-27% (288-296 mL/gVS). The kinetic study shows that the methane production rate was also 19-24% higher. Although similar results for tests B1-B2-B3, the highest productivity and production rate were for test B2, performed at 200ºC for 5 minutes (increase of 27% in the methane yield), corresponding to a severity factor (log R_0) of 3.64.

These results prove the effectiveness of the steam explosion pre-treatment, and concur with those obtained by other authors. The study published on methane production from steam-exploded wheat straw [21] agrees with the results obtained here. Bauer et al. (2009) [21] increased methane production from 275 to 331 mL/gVS when treating the straw at 180ºC for 15 minutes. [26] have previously optimized the pre-treatment conditions to a severity factor in the range 3.25-3.53, finding the optimum at 200ºC and 5minutes. This optimal agrees with the one here obtained.

3.3 Series C: Influence of water impregnation time on thermal hydrolysis

This series was conducted with 3-5 cm wheat straw thermally pretreated at 200ºC for 5 min (according to the optimum results for series A and B), with the objective of evaluating if water impregnation of wheat straw had any positive effect on the pre-treatment. The hypothesis that supports the theoretical possibility of increasing the steam explosion effect by washing the straw is the chance of the water to penetrate in the biomass structure, leading to a possible stronger lysis effect by steam explosion during the pressure drop.

Figure 6.3.2.4 and Table 6.3.2.5 present the results for the methane yield and kinetic parameters for series of tests C. The results show a negligible influence of the washing time on the thermal steam explosion pre-treatment, as the results obtained were very similar in the different tests. Only the kinetics showed to be slightly faster, but negligible. Therefore, the water added probably did not penetrate in the wheat straw structure, and did not help to disrupt the fibrils in the decompression step.

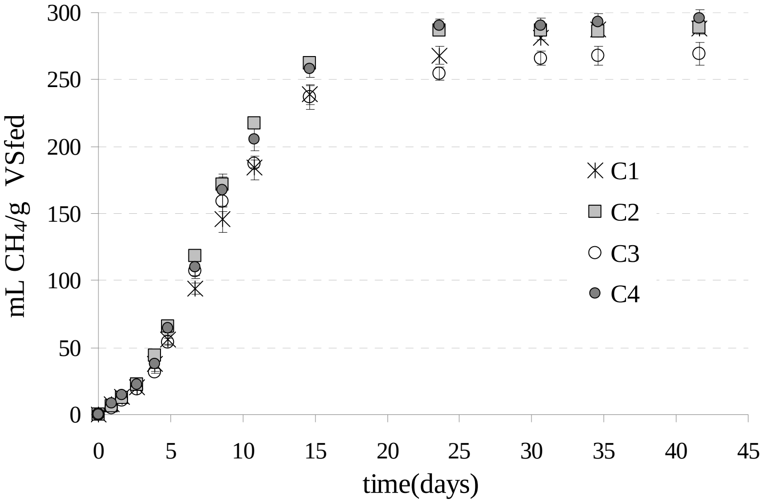

Figure 6.3.2.4. Methane yield for series C

Table 6.3.2.5. Results for methane yield and kinetic parameters for series C

Parameter	C1	C2	C3	C4
P (mL CH_4/gVS) [a.]	316	315	293	323
Rm (mL CH_4/gVS.d) [b.]	23.4	28.2	24.4	26.7
λ (day) [c.]	1.3	1.3	1.4	1.3
R^2	0.971	0.963	0.962	0.964

[a.] P: maximum methane production; [b.] Rm: maximum biogas production rate; [c.] λ: lag time (according to Equation 6.3.2.2)

Although according to Jakoviak et al. (2011) [16], the humidity of the biomass may cause differences on the contents of cellulose and hemicellulose of wheat straw, the evaluation of the chemical composition of the straw in terms of lipids, carbohydrates and proteins would again be determining to confirm any hypothesis.

4. Conclusions

The methane production of 30-50 mm wheat straw pieces was 10.4% higher than the powder <1 mm. Therefore, for process performance and economics, cutting is desirable to milling. Thermal pre-treatment enhanced methane production by 19-24% for temperatures in the range 170-220ºC and 1-15 min heating time, being the optimum for 200ºC and 5 min, which increased methane yield by 27% (from 233 to 296 mL CH_4/gVS_{fed}). The impregnation of straw with water showed a poor positive effect in the BMP tests, but no effect on thermal steam explosion, apart from a clear worsening of the process economics if water was added.

Acknowledgments

This work was financially supported by the company Cambi (project “Thermal hydrolysis of solid wastes”). The research group is “Grupo de Excelencia GR76 de la Junta de Castilla y León” and member of the Consolider-Novedar framework.

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Apartado 6.4

Hidrólisis térmica de purines de cerdo: *“Thermal Hydrolysis pretreatment to enhance biodegradability of the separated solid fraction of pig slurry.”*

Este apartado se describe en el artículo que sigue, correspondiente a una publicación enviada a la revista "Waste Management".

A continuación se recoge dicho artículo, incluyéndose una copia de la publicación en el capítulo de "Anexos".

Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure

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Abstract

The assessment of the biodegradability of thermal steam-exploded pig manure was performed compared to untreated samples. The pre-treatment was performed under different combinations of temperature and time, ranging 150-180ºC and 5-60 minutes, and used as substrate in a series of batch biochemical methane potential (BMP) tests. Results were analyzed in terms of methane yield, kinetic parameters and severity factor. In all the pre-treatment conditions, methane yield and degradation rates increased when compared to untreated pig slurry. An ANOVA study determined that temperature was the main factor, and the optimum combination of temperature - time of pretreatment was 170 ºC - 30 minutes, doubling methane production from 159 to 329 mL CH_4/gVS_{fed}. These operation conditions correspond to a severity factor of 3.54, which was considered an upper limit for the pretreatment due to the possible formation of inhibitory compounds, hindering the process if this limit is trespassed.

Keywords: biochemical methane potential, thermal hydrolysis, pretreatment, methane yield, pig slurry; steam-explosion

1. Introduction

In Spain, currently the second largest producer of pig manure in the European Union (PNIR, 2007-2015), manure management has become an environmental issue. The traditional application of manure is as land fertilizer (Schöder, 2005), contributing to maintaining the soil organic carbon and nutrients stocks. However, due to the intensification of livestocks production, in many areas the organic waste nutrients exceed the requirement for crop production (Wnetrzak et al., 2013), resulting in groundwater contamination, nitrates leaching and eutrophication. Therefore, any kind of treatment for pig wastes must be implemented according to the environmental legislation, such as the EU Nitrates Directive (S.I. NO. 610, 2010).

The valorization of the organic matter content in pig manure to biogas through anaerobic digestion (AD) is a very interesting option (Krishania et al., 2013; Mata-Alvarez et al., 2000), although ammonia inhibition issues have to be taken into account for considering manure as a sole substrate (Hansen et al., 1998). However, similar to other types of organic wastes, biogas production from pig manure is relatively low: from 290 to 550 L CH_4/kg of organic matter (Burton and Turner, 2003), due to the limiting hydrolysis step of the fiber content (Menardo et al., 2012). Some treatment options are reported to increase AD performance, such as acidification (Moset et al., 2012; Sutaryo et al., 2013) or separation of solid and liquid fractions (Fangueiro et al., 2012; Møller et al., 2007).

Thermal pre-treatment appears as a very interesting option and a potential solution for a large quantity of lignocellulosic biomass. The use of a thermal pre-treatment to enhance the anaerobic digestion of sewage sludge is reported in several references (Pérez-Elvira et al., 2011; Bougrier et al., 2008), and has been developed full scale. However, the application to other organic wastes such as agricultural wastes (Ferreira et al., 2013; Qiao et al., 2011) or manure is very recent, and still open to research. Some references can be found concerning thermal pretreatment to chicken manure (Ardic and Tarner, 2005; Bujoczek et al., 2000), swine manure (Mladenovska et al., 2006; Chae et al., 2008), dairy manure (Yoneyama et al., 2006; Rico et al., 2011; Rico et al., 2012) and pig manure (Bonmati et al., 2001; Cuetos et al., 2008; Carrère et al., 2009; Menardo et al., 2011). In the references found on thermal pre-treatment of manure the study was performed considering only the effect of temperature (with or without chemicals), but no evaluation on the influence or optimization of temperature-time combinations are reported.

Finally, the application of any thermal technology requires to concentrate the waste (Pérez-Elvira & Fdz-Polanco, 2012). Several references can be found about separation of solid and liquid fractions of pig slurry in order to economize transport or increase the energy potential through biogas production (Møller et al., 2007; Nolan et al., 2012; Xie et al., 2012).

The aim of this study was to evaluate the methane yield of steam exploded pig slurry (separated solid fraction of pig manure) under different temperature-time combinations, compared to a control of untreated slurry. BMP tests were performed and kinetic parameters were evaluated.

2. Material and Methods

2.1 *Manure samples: thickening and characterization*

Pig slurry was collected from a piggery in Segovia (Spain) and characterized before ("original sample") and after centrifugation at 5000 rpm for 5 min ("solid fraction"). Table 6.4.1 presents the results from the analytical characterization.

Table 6.4.1 Average characteristics of the original sample and solid fraction of pig manure (before and after centrifugation, respectively).

Parameter		**Original sample**	**Solid fraction**	**Units**
Total solids	TS	46.6 ± 2.1	166.4 ± 0.2	g/kg
Volatile Solids	VS	36.8 ± 2.7	138.6 ± 0.2	g/kg
Percentage of VS	% VS	79	83	-----
Chemical oxygen demand	COD	54.20 ± 0.8	197 ±3	gO_2/kg
Total kjeldahl nitrogen	TKN	7.40	6.05	gN/kg
Total organic carbon	TOC	6.29	7.48	% weight
Ratio C/N	C/N	8.5	12.4	-----
Ammonium	NH_4^+	4671	-----	gNH_4^+-N/g
Ratio COD/VS	COD/VS	1.47	1.42	-----

As expected, the concentrated pig slurry (manure) presented a higher percentage of volatile solids, which means a higher content of organic matter. The C/N ratio increased when compared to the original sample, which allows better conditions for the treatment.

2.2 *Thermal pretreatment pilot plant and operation conditions*

As shown in Figure 6.4.1, the thermal hydrolysis plant consisted of a reactor (2L) connected to a boiler by a control valve (V1) and to a flash tank (5L) by a decompression valve (V2). The operation was batch: 250g of pig manure were fed to the reactor, and then heated with steam from the boiler (180ºC, 10 bar) for the desired period of time. Once completed the operation time, the steam inlet (V1) is closed and the decompression valve (V2) is opened in a sudden decompression, releasing the hydrolysed pig slurry to the atmospheric flash tank. Before starting the experiments, the reactor was pre-heated for approximately 5 min at the same temperature selected for the pretreatment, in order to minimize condensation.

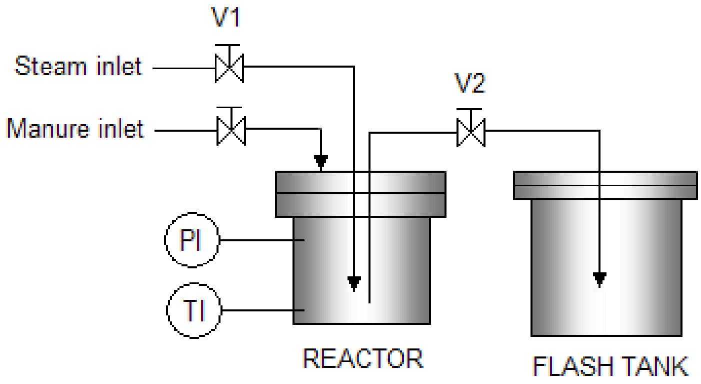

Figure 6.4.1 – Thermal steam-explosion pilot plant

Different pretreatment conditions were tested varying both temperature (ranging from 120-180ºC) and time (ranging from 5-60 minutes), in a total of 15 different operation conditions (Table 6.4.2).

Table 6.4.2 Thermal conditions applied, experimental results and kinetic parameters for the different experiments performed

Experimental Results					**Kinetic Parameters**			
TH i	**T (ºC)**	**t (min)**	**Severity Factor ($\log R_0$)**	**FN**	**Rm mL CH_4/gVS$_{fed}$.d**	**λ (d)**	**P mL CH_4/gVS$_{fed}$**	**R square**
TH0	0	0	0.00	1.00	32.1	0.22	159	0.9852
TH1	120	5	1.29	1.26	31.6	0.10	200	0.9547
TH2	120	15	1.76	1.59	41.2	0.15	253	0.9737
TH3	120	30	2.07	1.63	48.2	0.12	259	0.9684
TH4	120	60	2.37	1.67	70.8	0.22	265	0.9821
TH5	150	5	2.17	1.70	47.9	0.21	271	0.9825
TH6	150	15	2.65	1.75	55.0	0.25	278	0.9876
TH7	150	30	2.95	1.72	78.3	0.32	273	0.9893
TH8	150	60	3.25	1.72	116.3	0.38	274	0.9875
TH9	170	5	2.76	1.84	63.1	0.45	292	0.9973
TH10	170	15	3.24	1.93	72.3	0.47	308	0.9950
TH11	170	30	3.54	2.07	106.1	0.45	329	0.9868
TH12	170	60	3.84	1.53	88.3	0.45	244	0.9844
TH13	180	5	3.05	1.99	70.6	0.39	317	0.9863
TH14	180	15	3.53	1.77	62.4	0.45	282	0.9971
TH15	180	30	3.83	1.70	87.7	0.47	271	0.9839

The combination temperature and time of pretreatment define the severity factor (log R_0, eq. 6.4.1). This parameter is most widely accepted for steam pretreatments (Hendriks and Zeeman, 2009) to express the severity of the pretreatment.

$$\log R_0 = \log\left(t.exp\left(\frac{T-100}{14.75}\right)\right) \qquad (6.4.1)$$

in which *t* is the time (min) and *T* the temperature (°C), 100 is the base temperature (100ºC), and 14.75 is the activation energy based on the assumption that the reaction is hydrolytic and the overall conversion is first order (Xu et al., 2011). This expression only takes into account time and temperature, and does not consider the effect of the flash. The study of this effect was not assessed in this paper.

Theoretically, the more severe the pretreatment, the more organic matter is made available for digestion. However, very severe pretreatments can lead to formation of inhibitory compounds from the macromolecules, driving to an indirect relationship between the severity factor and the biodegradability. Therefore, there should be an optimum value for the severity factor.

2.3 *Anaerobic biodegradability*

Biochemical methane potential (BMP) tests were carried out in triplicate to assess the pig slurry biodegradability before and after the different pretreatment conditions applied, following standardized methodology (Angelidaki et al., 2009). A control test without substrate was included in order to check the methanogenic activity of the inoculum. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1±0.3ºC), with constant mixing in a shacker desk.

The anaerobic inoculum used was taken from a pilot sludge digester treating activated sludge (containing 12 $gVS.kg^{-1}$) and pre-incubated for four days (35.1±0.3ºC) in order to minimize its residual biodegradable organic matter content.

Borosilicate glasses of 300mL volume were used in the BMP tests, with a reaction volume of 110mL in order to have enough headspace for biogas accumulation. The substrate/inoculum (S/I) ratio selected was 0.5 $gVS.(gVS)^{-1}$, as suggested by Neves et al. (2004) and Angelidaki et al. (2009).

Biogas production was measured manually by a pressure transmitter (ifm, PN5007, range 1 bar) in the headspace of each reactor. From the biogas production curves, the specific methane yield (mL CH_4/gVS_{fed}) was calculated at test-day 20 under standard temperature and pressure conditions (STP – 0ºC, 1 atm) defined by IUPAC (International Union of Pure Applied Chemistry), by dividing the methane production due to the substrate (once subtracted the production due to the inoculum) by the quantity of volatile solids of substrate fed to the test ($mL_{substrate}$ x g $VS/mL_{substrate}$).

2.4 *Analytical Methods*

Substrates, inoculum and digestates were characterized in all the experiments. Total and volatile solids (TS and VS, respectively) and total kjeldahl nitrogen (TKN) were measured following the procedures given in the *Standard Methods for Examination of Water and Wastewater* (APHA et al., 2005). Chemical oxygen demand (COD) was determined according to standard UNE 77004:2002 based in the dichromate method. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

2.5 *Data analysis and kinetic approach*

Apart from obtaining the specific methane yields (mL CH_4/gVS$_{fed}$), a kinetic approach was also employed to analyze the obtained data. The kinetics of methane production were calculated using a reaction curve-type model (eq. 6.4.2), applied successfully in other studies regarding anaerobic biodegradability tests (Ferreira et al., 2013).

$$B = P.\left(1 - exp\left(\frac{-Pm(t \quad \lambda)}{P}\right)\right) \qquad (6.4.2)$$

in which B is the methane production (mL CH_4/gVS), P is the maximum methane production (mL CH_4/gVS), R_m is the maximum methane production rate (mL CH_4/gVS·d), λ is the lag time (d) and t is the time of the assay (d). The data were analyzed with Statgraphics®.

Finally, to evaluate the influence of temperature and time of pretreatment on methane production, the results obtained were compared by the analysis of variance methodology (ANOVA), using Microsoft Excel®, with a confidence level of 95%.

3. Results and Discussion

3.1 *Batch tests and methane yield*

Figure 6.4.2 presents the evolution of methane productivity (mL CH_4/gVS_{fed}) in all the BMP assays performed, compared to the control untreated substrate (TH0). For better comparison, Table 6.4.2 present the final specific methane yield improvements respect the control as normalized production of methane (FN), defined as the ratio at day 20 between the production of methane for the treated and untreated waste, $(\text{mL } CH_4)_{THi}/(\text{mL } CH_4)_{untreated}$.

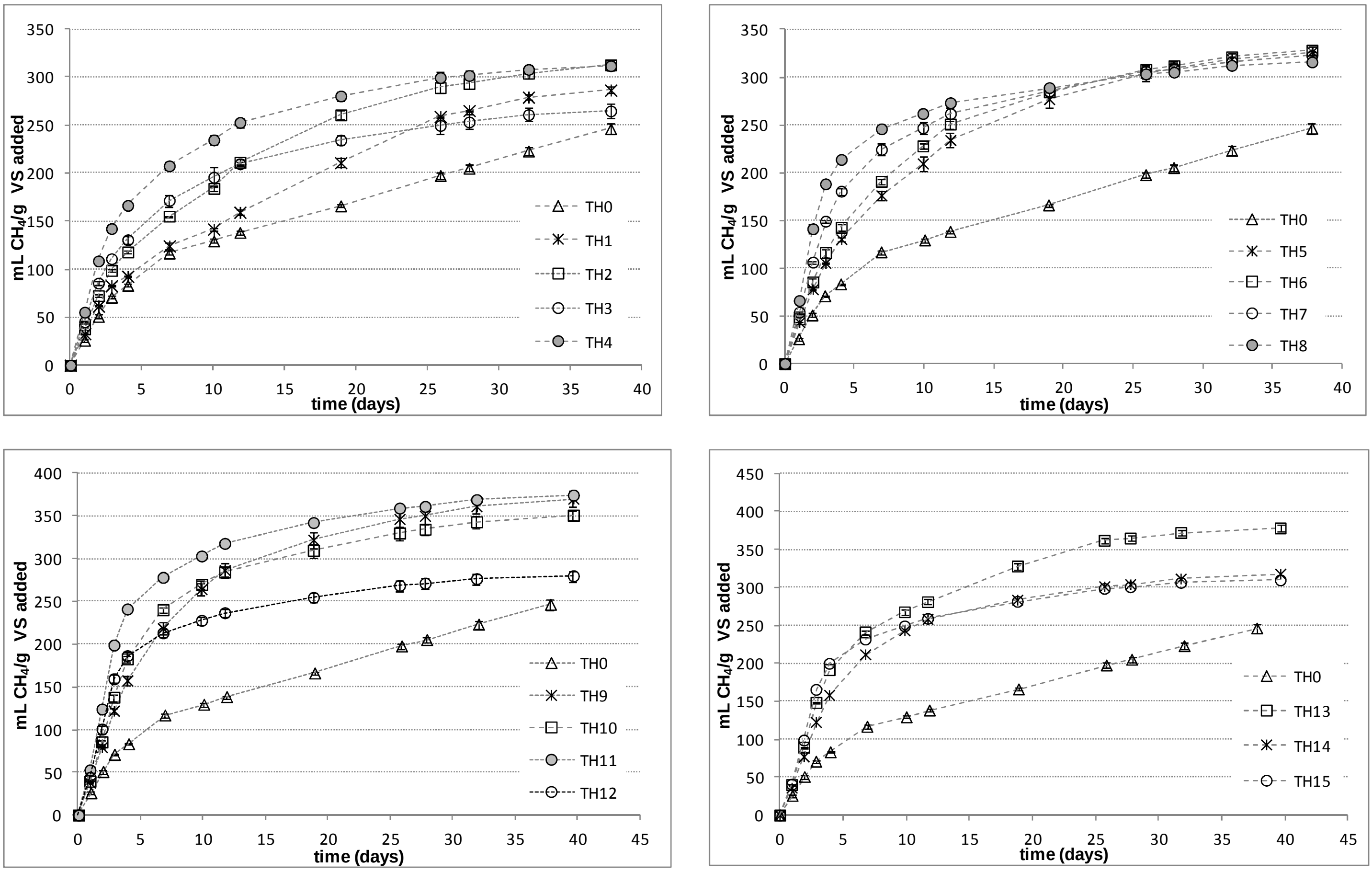

Figure 6.4.2 – BMP assays for the different experimental conditions applied

3.2 *Evaluation of temperature-time combinations*

An initial evaluation of the results presented in the “Experimental results” column of Table 6.4.2 show that all the pre-treatments performed (TH1-TH15) enhanced the initial biodegradability of the pig slurry (TH0), from 26% (120ºC, 5 min) to 107% (170ºC, 30 min), being the latter the best pre-treatment condition evaluated. Comparing the influence of temperature and time, it can be observed a different behaviour depending on the temperature level. For low temperatures (120ºC), the influence of pre-treatment time was the most noticeable. For moderate temperatures (150ºC), the influence of the pre-treatment time was not so strong. For high temperatures (170 and 180ºC), time played a crucial role from the point of view of inhibition. Pre-treatment times over 30 minutes at 170ºC or over 15 minutes at 180ºC caused a reduction in methane yield, probably due to the formation of inhibitory compounds.

Based on this qualitative analysis, a quantitative analysis of variance was performed. The data concerning pre-treatment time of 60 min were not considered for this study, as methane yield was mostly inhibited. The results of the ANOVA study showed that in all cases temperature caused significant statistical difference between data (F_{ratio} = 6.29, $F_{critical}$ = 4.76), while pre-treatment time did not (F_{ratio} = 2.81, $F_{critical}$ = 5.14). This indicates that, when dealing with both variables, temperatures should be considered as the main parameter as the basis to define the best pre-treatment time.

Figure 6.4.3 presents a graphical approach of the effect of both temperature and time on FN. It can be observed that the best improvements in methane yield are centered in the combination 170ºC, 30 min, which is in accordance to the globally accepted values regarding thermal hydrolysis of sludge (Fdz-Polanco et al., 2008). This suggests that these thermal hydrolysis conditions are the optimum for enhancing the methane yield of concentrated pig slurry.

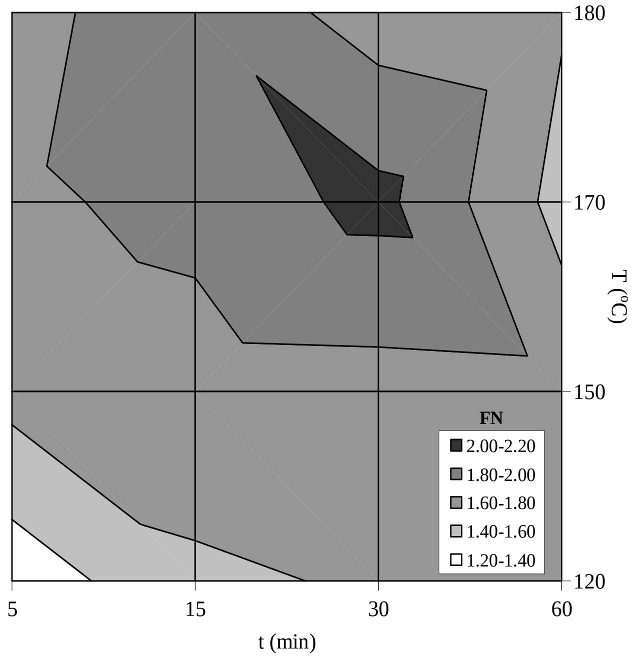

Figure 6.4.3 – Effect of temperature and time of pretreatment on FN. Darker areas mean regions in which values of FN are higher

3.3 Evaluation of kinetic parameters

The kinetic parameters obtained by fitting equation 6.4.2 to the experimental data on methane production are presented in the “Kinetic parameters” column of Table 6.4.2. The results obtained concerning the maximum methane production (P) match with those previously discussed: increase for temperature and time increase, but decreasing trend for the longest times at temperatures above 170ºC. However, maximum methane production rates (R_m), seemed to differ slightly from this trend. The highest value of R_m was obtained for 150°C, 60 min, and lower R_m values were obtained for higher temperatures. And, again, pre-treatment times over 30 minutes for 170ºC and over 15 minutes for 180ºC caused a reduction in methane production rates.

Figure 6.4.4 present the effect of temperature and time on R_m. Although similar to Figure 6.4.2 with respect to the optimum (170ºC, 30 minutes), the trend for higher temperature-time values is different. These results suggest that inhibition of the maximum methane production is not necessarily coupled to lower degradation rates in the same levels. Even with the formation of refractory compounds due to high temperatures and pretreatment times, those conditions might still be able to improve rates, leading to reduced size of digesters as one possible advantage. However, a precise choice would depend on economic studies that take into account several variables and the process as a whole.

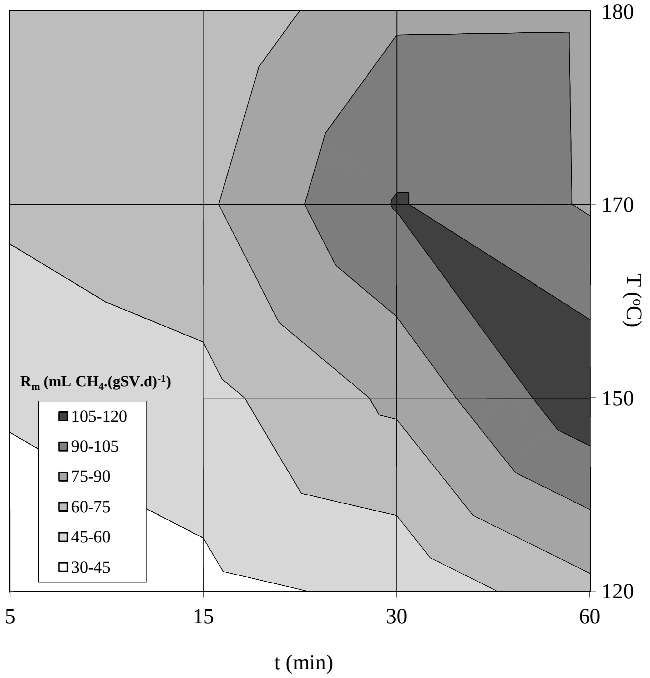

Figure 6.4.4 – Effect of pre-treatment temperature - time combinations on the methane production rates (R_m). Darker areas mean regions in which values of R_m are higher

3.4 Evaluation of the severity factor

Figure 6.4.5 presents the relationship between the severity factor and the normalized production of methane (FN). The influence of the severity factor on the response of the methane yield presents some differences when temperature and time change. For temperatures of 120 and 150°C, it is clear by Figure 6.4.5 that FN always increases with the severity factor. However, for the higher temperatures of 170 and 180°C, there is a limit in the severity factor that, once surpassed, a reduction in FN occurred. According to Figure 6.4.5 and Table 6.4.2, the optimum value for the severity factor would be 3.54 for a temperature of 170°C. For a temperature of 180°C, however, this severity factor led to lower values of FN. For higher values of the severity factor, inhibition in methane production was observed. This suggests that a severity factor of 3.54 could be considered an upper limit in which some instability in performance may be expected depending on operational conditions.

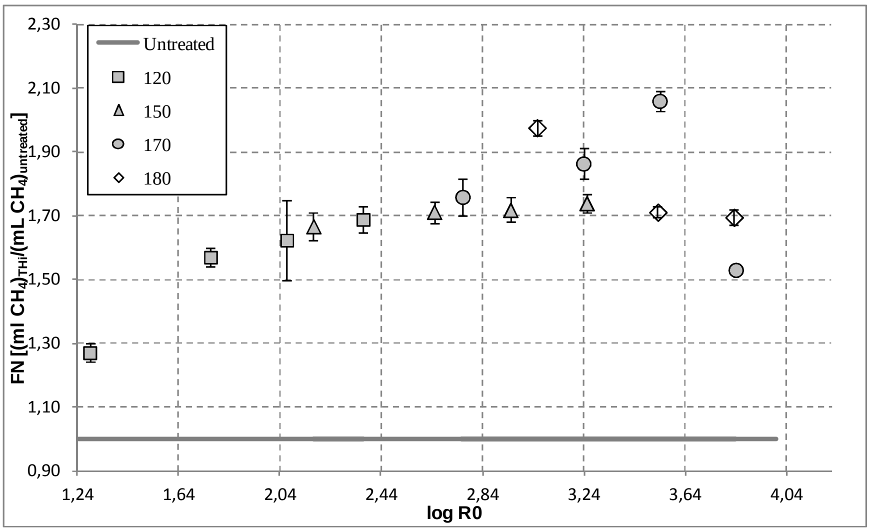

Figure 6.4.5 - Normalized methane productivity (FN [(mL CH_4)$_{THi}$/(mL CH_4)$_{untreated}$]) with respect to the severity factor (log R_0)

Conclusions

The influence of thermal pretreatment parameters (temperature and time) on the anaerobic biodegradation of the solid fraction of pig slurry was evaluated. All the conditions tested were better than the untreated condition, which means that the thermal pretreatment improved the anaerobic digestion of this type of waste, not only concerning biodegradability, but also degradation rates. Results suggested that temperature has a greater effect on methane yield than pretreatment time, and that the best combination of parameters would be 170°C and 30 min, which was able to maximize methane production up to 200% when compared to untreated samples (from 159 to 329 mL CH_4/gVS$_{fed}$). This corresponds to a severity factor of 3.54, which seemed to be an upper limit not to be trespassed to avoid the formation of inhibitory compounds.

Acknowledgments

This work was financially supported by the company Cambi$^{®}$, project “Thermal hydrolysis of solid wastes”. The group of Valladolid University is *Grupo de Excelencia GR 76 de la Junta de Castilla y León* and member of the Consolider- Novedar framework (Programa Ingenio 2010).

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Apartado 6.5

Hidrólisis térmica de lodo de EDAR: *"Thermal pretreatment and hydraulic retention time in continuous digesters fed with sewage sludge – Assessment using the ADM1."*

Este apartado se describe en el artículo que sigue, correspondiente a una publicación en la revista "Bioresource Technology".

"Theo S.O. Souza, Liliana Catarina Ferreira, Ieva Sapkaite, Sara I. Pérez-Elvira, Fernando Fdz-Polanco, 2013. Thermal pretreatment and hydraulic retention time in continuous digesters fed with sewage sludge: Assessment using the ADM1. Bioresource Technology. 148, 317-324."

A continuación se recoge dicho artículo, incluyéndose una copia de la publicación en el capítulo de "Anexos".

Thermal pretreatment and hydraulic retention time in continuous digesters fed with sewage sludge: Assessment using the ADM1

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Abstract:

Thermal pretreatment is an interesting technique not only for increasing sludge biodegradability, leading to higher methane productivity, but also degradation rates, allowing full-scale plants to reduce the size of digesters. In this study, the Anaerobic Digestion Model No. 1 (ADM1) was used as a tool to assess the effects of thermal pretreatment and hydraulic retention time (HRT) on the performance of three pilot-scale digesters fed with mixed sludge with/without pretreatment applied to the waste activated sludge fraction. Calibration procedures using batch tests showed an increase of up to five times in the model disintegration coefficient due to the pretreatment, and the validations performed presented good accuracy with the experimental data, with under/overestimation lower than 15% in both average and global accumulated CH_4 productions. Therefore, the ADM1 demonstrated its feasibility and usefulness in predicting and assessing the behavior of the digesters under these conditions.

Keywords: ADM1, anaerobic digestion, modeling, sludge pretreatment, thermal hydrolysis

1 INTRODUCTION

Wastewater treatment plants (WWTPs) based on the activated sludge system as the core unit are globally spread, due to its reliability and efficiency in a wide range of environmental and operational conditions. However, this alternative presents two main economical drawbacks: aeration costs and large volume of sludge to be disposed. The disposal of primary and waste activated sludge (PS and WAS, respectively) may represent up to 50% of the total operating costs of WWTPs (Appels et al., 2008), and thus attention must be strongly directed in this regard. Among the procedures for sludge stabilization, anaerobic digestion (AD) is commonly applied, with advantages including lower costs and conversion of organic matter to methane, which can be used for energy generation. Sludge biodegradability and degradation rates are a matter of concern, though, and inherently linked to AD energy integration and economic viability. WAS is mainly composed of microbial cells/flocs, presenting low biodegradability; especially when produced by activated sludge systems operated with extended aeration; in contrast, PS is more biodegradable (Carlsson et al., 2012). Nevertheless, both may be mixed and thickened for further treatment (Carrère et al., 2010). Increasing the degradation extent and rates, leading to improved methane production, solids reduction and overall process optimization, is therefore of paramount importance in sludge management.

Several sludge pretreatment techniques have been studied in the past years, with the purpose of improving AD of sludge and other substrates. They include thermal, mechanical, chemical, biological, wet oxidation, freeze/thaw, microwave and pulsed electric field pretreatments (Carrère et al., 2010; Bordeleau and Droste, 2011; Carlsson et al., 2012). Among the available alternatives, thermal hydrolysis has been shown to be of particular interest to improve the AD of WAS (Li and Noike, 1992; Fdz-Polanco et al., 2008). Thermal hydrolysis may account for an improvement of up to 100% in biogas production (Li and Noike, 1992; Carrère et al., 2010), with additional solids reduction, pathogens elimination (Pérez-Elvira et al., 2011) and increase in dewaterability (Neyens and Baeyens, 2003). Increase in biodegradability and degradation rates, and subsequent improvements in methane production, are related mainly to COD solubilization when thermal pretreatment is applied (Carlsson et al., 2012). Temperatures usually between 160-180^{o}C, pressures of 600 to 2500 kPa and treatment times of 30-60 min (Carrère et al., 2010) are able to disrupt cell walls and flocs, solubilizing organic matter and increasing the hydrolytic limiting-step considered responsible for low biodegradability and degradation rates of WAS (Li and Noike, 1992). Aside from the benefits already mentioned, hydraulic retention time (HRT) of digesters can also be reduced (Graja et al., 2005).

The assessment of thermal hydrolysis pretreatment effects on the AD of sludge, as well as the influence of decreasing the HRT of digesters in such conditions, can be done not only through regular monitoring of physicochemical parameters. Modeling is a powerful tool to provide additional information about biological processes, improving the understanding of the system, the formulation and validation of hypotheses and being able to predict system's performance (Donoso-Bravo et al., 2011a). Among the wide collection of AD models developed in the last decades, IWA's Anaerobic Digestion Model No. 1 (ADM1) is a structured and more complete approach, embracing several biochemical steps, as well as physicochemical phenomena (Batstone et al., 2002). It has been applied to the AD of several types of waste (Blumensaat and Keller, 2005; Galí et al, 2009; Mairet et al., 2011) and has potential for predicting effects of sludge pretreatments on AD (Souza et al., 2013), including thermal pretreatment (Phothilangka et al., 2008; Ramirez et al., 2009).

This study aimed to evaluate the effects of thermal pretreatment on the AD of sewage sludge, including the possibility of reducing HRT of digesters. The ADM1 was calibrated using batch tests data and employed as a tool for assessing the behavior of three continuous digesters, two of them fed with a mixture of raw PS and thermally pretreated WAS at different HRTs, and one used as a control and fed with a mixture of raw PS and raw WAS.

2 MATERIAL AND METHODS

2.1 Waste characteristics

PS and WAS were obtained from the WWTP of Valladolid, Spain. Both were concentrated and mixed at a 50/50% ratio (gVS/gVS), with a final feeding concentration of approximately 40 gVS.L^{-1}. The procedure and VS feeding concentrations were the same regardless of whether WAS was pretreated or not. As a result, two types of substrate were obtained: S1, consisting of a mixture of PS and thermally pretreated WAS (TPWAS); and S2, consisting of a mixture of PS and raw WAS (RWAS). S1 and S2 were characterized through systematic monitoring of the digesters' feeding for one month, and average parameter values are shown in Table 6.5.1.

Table 6.5.1. Average waste characteristics.

		S1	S2
Composition	(gVS/gVS)	PS (50%) + TPWAS (50%)	PS (50%) + RWAS (50%)
pH	-	6.09 ± 0.07	6.38 ± 0.14
COD	$(g.L^{-1})$	60.17 ± 2.02	62.00 ± 2.65
COD(s)[a]	$(g.L^{-1})$	15.46 ± 4.74	5.50 ± 2.68
TS	$(g.L^{-1})$	57.12 ± 4.73	59.79 ± 4.98
VS	$(g.L^{-1})$	37.75 ± 2.35	40.22 ± 1.69
TKN	$(gN.L^{-1})$	2.71 ± 0.13	2.84 ± 0.20
TKN(s)[a]	$(gN.L^{-1})$	1.27 ± 0.03	0.34 ± 0.11
NH_4^+-N	$(gN.L^{-1})$	0.31 ± 0.03	0.15 ± 0.1
Proteins	(%bCOD)[b]	40	40
Carbohydrates	(%bCOD)[b]	30	30
Lipids	(%bCOD)[b]	30	30

Nomenclature:
TS: Total Solids; VS: Volatile Solids; TKN: Total Kjeldahl Nitrogen
[a] Soluble fraction
[b] Percentage of the biodegradable COD

2.2 Continuous digesters and thermal pretreatment

Three identical 200-L digesters (A, B and C) were operated at 35ºC to treat sludge from the WWTP. Digester A and B were fed with substrate S1, and digester C was kept as a control and fed with substrate S2 (Table 6.5.1). Digesters A and C were operated at a HRT of 20 days, while digester B was operated at the reduced HRT of 10 days. WAS was concentrated until 12-14% TS using a commercial centrifuge and then thermally pretreated in a Continuous Thermal Hydrolysis (CTH) industrial prototype operating with of 40 min, temperature of 170ºC and pressure of 7.6 bar followed by steam explosion to atmospheric pressure. The main elements of the CHT prototype were preheated receiving steam from flash, reactor with direct injection of steam at 10 bar and flash tank at atmospheric pressure. An overview of the experimental set-up is presented in 6.5.1.

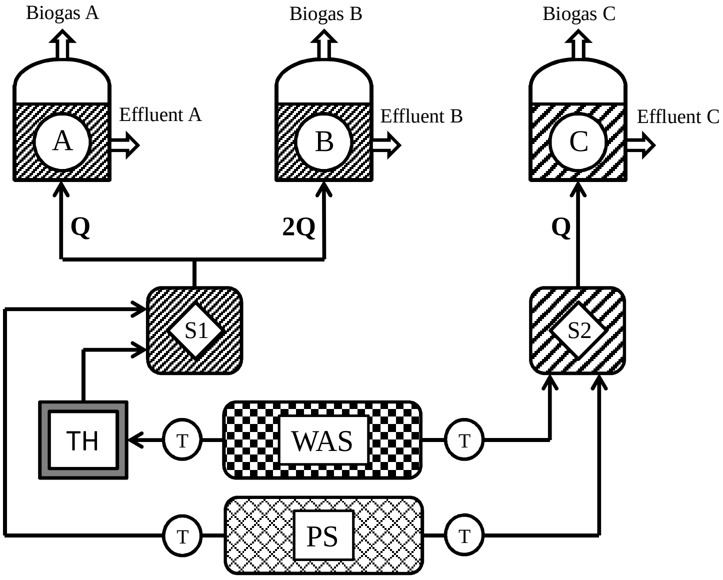


Figure 6.5.1. Overview of the experimental set-up. PS: primary sludge; WAS: waste activated sludge; T: thickening; TH: thermal hydrolysis; S1: substrate type 1; S2: substrate type 2; Q: flow rate.

Digesters were operated in three distinct phases, amounting for approximately 160 days of operation. Phase I consisted of a startup period of 50 days, for which simulations were not done, due to the instability of the reactor in the period. Phase II regarded the stable operation of the digesters, for approximately 80 days, with a feeding substrate of 40 $gVS.L^{-1}$, both for S1 (digesters A and B) and S2 (digester C). The final 30-day period was defined as phase III, in which the concentration of the feeding was increased to 55 $gVS.L^{-1}$. To eliminate punctual variability, as well as noise in the simulations, and for better comparison with experimental results from the digesters, a moving average considering a factor of 3 days was applied to inlet and outlet data.

2.3 Batch tests

Biochemical methane potential (BMP) tests were carried out in order to assess the sludge biodegradability and to provide data for model calibration. This was performed in three different series, each representing the current situation of digesters A, B and C, by combining the mixed sludge fed to each digester (substrate) with the corresponding effluent digested sludge (inoculum). This procedure was done for three timed samples collected throughout one month in phase II, and average results were used as dats source for further calibration.

All tests were made in triplicate at mesophilic conditions in a thermostatic room (35.1 ± 0.3ºC) with constant mixing in a shaker desk. The methodology used was the one suggested by Angelidaki et al. (2009). The substrate/inoculum ratio (S/I) used was 0.5 gVS/gVS, as recommended by Neves et al. (2004). A control test without substrate was included in order to account for the methanogenic activity of the inoculum. All the assays were finished when the methane production was below 5% of the total cumulative production.

The biogas volume was monitored by periodic measurements of the headspace pressure by a manually pressure transmitter (IFM, PN5007, range 1 bar), and was expressed as methane yield (mL $CH_4.(gVS_{added})^{-1}$), under standard temperature and pressure conditions (0 ºC, 1 atm).

2.4 Analytical methods

Unless specified otherwise, all analyses were performed in agreement with the *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 2005). Carbohydrates (as glucose) were measured according to Dubois et al. (1956), and lipids were determined using the Soxhlet extraction method. Proteins were calculated using NH_4^+ and TKN data (Girault et al., 2012). Biogas composition was measured by gas chromatography (Varian CP-3800 CG) using helium as carrier gas.

2.5 Model implementation

The ADM1 was implemented following the guidelines of Batstone et al. (2002), and modifications proposed by Rosén and Jeppsson (2006), using Matlab/Simulink®. The disintegration and hydrolysis parameters contained in the ADM1 (k_{dis}, k_{hydch}, k_{hydpr} and k_{hydli}) were estimated for each digester by minimizing a least-square cost-function using data obtained in BMP tests (section 2.3), as proposed by Souza et al. (2013). The remaining parameters were set according to Batstone et al. (2002). For model inputs, COD was fractioned considering substrate characterization (Table 6.5.1), following the procedures described by Souza et al. (2013). Biodegradable and inert COD fractions were defined according to the biodegradability obtained in BMP tests.

COD corresponding to biomass of the seven microbial populations contained in the ADM1 (X_{su}, X_{aa}, X_{fa}, X_{c4}, X_{pro}, X_{ac}, X_{h2}) were defined for BMP tests by performing a continuous simulation during a large period, starting with low concentrations of biomass and feeding the model with the same substrate as applied to the batch tests, until each biomass variable stabilized, as done by Girault et al. (2012), representing thus an overall proportion of microbial communities present in the inoculum. The same procedure was applied for simulating the continuous digesters.

With the set of hydrolysis parameters estimated for each digester, continuous simulations were performed considering variations in the flow rate and adjusting proportionately the COD fractioning to the inlet concentrations during operation. Simulations were then compared with experimental data to assess the effects of thermal pretreatment and HRT reduction on the digesters.

3 RESULTS AND DISCUSSION

3.1 Digesters performance

Table 6.5.2 shows the performance of digesters A, B and C considering the main parameters, in phases II and III. Phase I was not evaluated since it consisted of a startup phase, and comparison was not possible under startup conditions.

Table 6.5.2. Average performance of digesters A, B and C in phases II and III.

	Phase II			Phase III		
	A	B	C	A	B	C
CH_4 production ($L.d^{-1}$)	104 ± 17	162 ± 29	89 ± 20	120 ± 25	219 ± 57	117 ± 17
Effluent COD (g $O_2.L^{-1}$)	28 ± 2	30 ± 2	33 ± 3	29 ± 2	32 ± 2	32 ± 3
Effluent NH_4^+ (g $N.L^{-1}$)	1.4 ± 0.1	1.3 ± 0.1	1.0 ± 0.2	1.6 ± 0.2	1.6 ± 0.2	1.3 ± 0.1

Throughout the 80 days of operation in phase II, even though variations in the parameters were observed mainly due to feeding variability, in overall the average results were in accordance to the expected. CH_4 production was the lowest for digester C, presented a small improvement for digester A and a significant improvement for digester B. When compared to the control digester (C), digester A showed a 17% higher CH_4 production in phase II. This increase may appear low at first, but it must be considered that the thermal pretreatment was applied only to the WAS fraction of the substrate and, although a CH_4 production increase of 33% was reported in similar conditions (Pérez-Elvira and Fdz-Polanco, 2012), differences in the composition of PS and WAS in the mixed sludge, as well as operational variability may have caused the lower production. A much more significant CH_4 production in phase II was obtained in digester B, though, accounting for an average 82% enhancement when compared to the control. This shows the potential of thermal hydrolysis not only in increasing biodegradability and methane productivity of WAS, but also in allowing lower HRTs to be employed, and consequently reducing the size of digesters in full-scale applications.

Phase III showed a similar behavior regarding the comparison of digester B with the control (Table 6.5.2), but CH_4 production was almost the same for digesters A and C. In this phase, operation was much more unstable due to the increase in feeding concentration and operational problems, as discussed further in section 3.3, and a sharp drop in performance was observed for digesters A and B. Therefore, results were affected by such variations, hindering the evaluation based on average parameters.

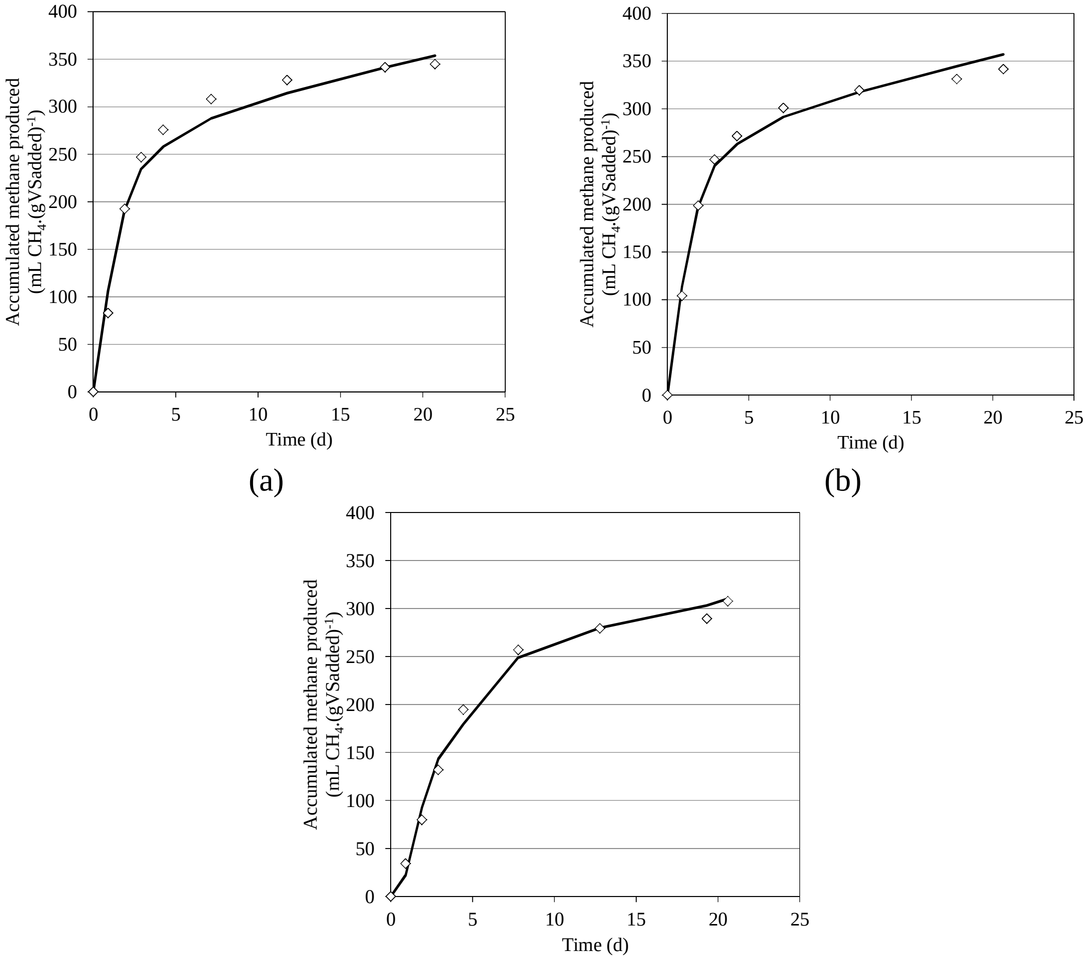
Effluent COD did not present sharp variations, and remained averagely in the range of 28-33 g O_2. L^{-1} for all digesters, according to Table 6.5.2. However, effluent ammonium presented itself in different levels, depending on the type of substrate fed to the digesters, with higher values for digesters A and B, fed with TPWAS. Indeed, thermal pretreatment is responsible for an increase in ammonium concentrations during anaerobic digestion, as also reported by Phothilangka et al. (2008), and this effect was even more pronounced in phase III. More detailed discussion about the behavior of the digesters in specific periods is presented in section 3.3, coupled with modeling analyses.

3.2 Calibration of disintegration and hydrolysis coefficients

The differences in CH_4 productivity given by the results of BMP tests are clearly visible in Fig. 6.5.2. Results corresponding to conditions applied to digester C (Fig. 6.5.2c) were not much higher than 300 mL $CH_4.(gVS_{added})^{-1}$, while tests corresponding to digesters A and B (Figs. 6.5.2a and 6.5.2b, respectively) reached 350 mL $CH_4.(gVS_{added})^{-1}$.

Regarding anaerobic biodegradability, BMP test resulted in values of 63.4, 61.4 and 53.7%, for samples corresponding to digesters A, B and C, respectively. Moreover, the initial kinetics of CH_4 production for digesters A and B were evidently faster than for digester C. This confirms the potential of thermal pretreatment in not only increasing the degradation extent of sludge in anaerobic digestion, but also the degradation rates. When comparing results for digesters A and B, though, no clear difference can be observed between the data points, indicating that the HRT did not affect the inoculum specific CH_4 productivity.

Calibration for ADM1 disintegration and hydrolysis coefficients produced optimum curves with good fits for experimental data, as can be seen in Fig. 6.5.2. Calibrated coefficients that generated the optimum fits for each case are shown in Table 6.5.3. Two separate behaviors could be inferred by the resulting coefficients: one associated to the disintegration coefficient k_{dis}, and the other related to the hydrolysis coefficients k_{hydch}, k_{hydpr} and k_{hydli} as a group. The coefficient k_{dis} was the most affected when comparing calibration results between the different digesters, as shown in Table 6.5.3. Five-fold and three-fold increases for this coefficient were obtained, when comparing digesters A and B with digester C, respectively. Increases for k_{hydch}, k_{hydpr} and k_{hydli} were less representative in both cases, though.



(a)

(b)

(c)

Figure 6.5.2. Experimental results of the BMP tests (◊) and model fit (continuous line) after calibration regarding ADM1 disintegration and hydrolysis coefficients for digesters A (a), B (b) and C (c).

The sharp increase of k_{dis} is in accordance to the expected effect caused by the pretreatment on the ADM1 disintegration step. Higher values of this coefficient represent that the destruction of bigger and complex particles is enhanced by the applied pretreatment, increasing the kinetics of this specific step. Similarly, Souza et al. (2013) obtained an increase from 0.24 d^{-1} to 5.60 d^{-1} in the coefficient k_{dis} when a low-thermal pretreatment was applied to sewage WAS. To describe properly the anaerobic digestion of thermally pretreated WAS, Phothilangka et al. (2008) had to change k_{dis} from 0.25 to

1.5, which is also in accordance with the obtained results. Regarding calibration for raw WAS, Batstone et al. (2009) and Donoso-Bravo et al. (2010) obtained single hydrolysis coefficients of 0.15-0.25 d^{-1}. In the case of the present study, coefficients in the range of 0.42-0.56 d^{-1} were obtained for digester C (Table 6.5.3), and those values are higher than the reported ones because in this study a mixture of PS and WAS was fed to the tests, therefore presenting faster kinetics due to the more biodegradable nature of the feeding.

The three hydrolysis coefficients, k_{hydch}, k_{hydpr} and k_{hydli}, varied less significantly among digesters and among themselves, with all three being in the same range for each case. Due to this characteristic, kinetics of the initial steps of anaerobic digestion in the ADM1 in this study presented themselves in two main stages for digesters A and B: a fast disintegration stage and a subsequent slow hydrolysis stage. In this sense, the numerical difference of k_{dis} between digesters A and B (Table 6.5.3) may not be important, since both represent non-limiting steps, with probably no significant physical meaning regarding their difference. For digester C, though, both disintegration and hydrolysis steps may play an important role in modeling, since they are all in the same range.

Table 6.5.3. Calibrated disintegration and hydrolysis coefficients for digesters A, B and C.

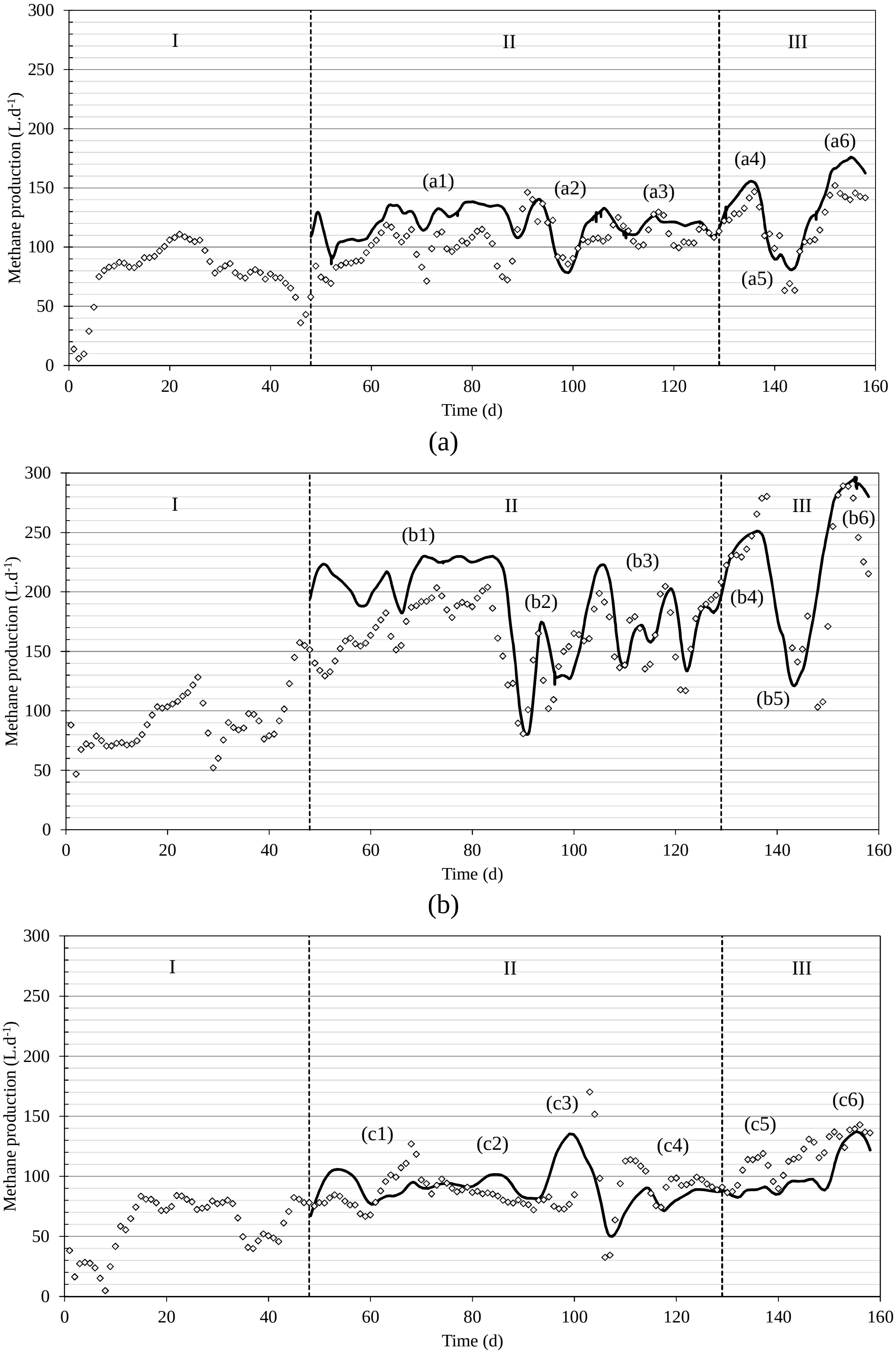
Digester	A	B	C
Substrate type	S1	S1	S2
HRT (d)	20	10	20
k_{dis} (d^{-1})	2.57	1.62	0.56
k_{hydch} (d^{-1})	0.66	0.78	0.51
k_{hydpr} (d^{-1})	0.78	0.79	0.44
k_{hydli} (d^{-1})	0.88	0.84	0.42
R^2	0.989	0.994	0.992

3.3 Validation using continuous digesters data

The experimental CH_4 production throughout the operation of digesters A, B and C, as well as the simulations using the calibrated model in each case, are presented in Fig. 6.5.3. Simulations followed really close the behavior of the digesters in some regions of the graphics, while in others some deviations were observed, as further discussed. Due to the instability of the startup phase (phase I), simulations are not presented in the graphics or discussed for this phase.

For digesters A and B, the initial regions of phase II, (a1) and (b1), were characterized by an overestimation of the CH_4 production, as can be seen in Figs. 6.5.3a and 6.5.3b. A similar, but minor, effect was also observed for digester C, in the region (c1) of Fig. 6.5.3c, but embracing model underestimation as well. The observed simulation results for the mentioned regions may be explained by the fact that those regions are immediately after the startup period of the digesters and, while some experimental instability were occurring in those regions, predictions were more optimistic for CH_4 production (mainly for digesters A and B), causing the differences. In this sense, it can be inferred that the model recovered faster from the instabilities of phase I than the digesters themselves. For digester C, region (c1) shows instability as well, which was not properly followed by the simulations, resulting in under and overestimation in this specific period.

After the initial periods of phase II, simulations predicted the behavior of the digesters with higher accuracy, which is evident mainly in regions (a3), (b3), (c2) and (c4) shown in Fig. 6.5.3. Predictions had good quality even when sharp experimental variations in CH_4 production were observed, such as the ones contained in regions (a2), (b2) and, in a lesser degree, (c3). The peaks and drops were related to the influent COD that presented a high variability in those regions and, since the same variations were fed as COD to the model, predictions also followed the tendencies, which showed good model robustness in this sense.



(a)

(b)

(c)

Figure 6.5.3. Validation of the calibrated model with respect to methane production, using data from digesters A (a), B (b) and C (c): (◊) experimental data, (–) simulation. Discontinuous vertical lines represent changes in operational phase, and codes in parenthesis are used to name different regions of the graphics for enhanced discussion.

Phase III presented an increase in CH_4 production for all digesters, due to increased feeding concentrations, and consequently higher organic loading rates. The improvement in CH_4 production was sustained during the whole phase for digester C, as shown in Fig. 6.5.3, but the same was not true for digesters A and B, which suffered a sharp drop in performance after approximately one week of operation in this phase, with a later recovery at the end of the period. Nonetheless, model predictions followed correctly this behavior, representing well the peaks (regions (a4), (a6), (b4) and (b6)) and drops of performance (regions (a5) and (b5)). Digester C responded faster to the increase in organic loading rates than the model, as can be seen in region (c5), and simulations only reached the higher levels of CH_4 production at the end of phase III (region (c6)).

The instability observed in phase III for digesters A and B were not caused by variations in the inlet COD as happened punctually in phase II, but the sharp drop in CH_4 production resulted from operational problems with the feeding, which was done with reduced flow rates for some days, decreasing CH_4 production in the period. Since the model takes into account the flow rates applied to the digesters, this phenomenon was accurately followed in the simulations. Digester C did not present this operational problem; therefore such a drop in performance was not detected.

Concerning the ammonium concentrations, the model was able to predict this parameter accurately as well. The simulated average ammonium concentrations in phase II were 1.49, 1.39 and 0.91 g $N.L^{-1}$ for digesters A, B and C, respectively. During phase III, those concentrations were 1.64, 1.69 and 1.15 g $N.L^{-1}$, in the same order of digesters. When compared to the average experimental data for this parameter, presented in Table 6.5.2, simulated values presented good performance, with average differences not higher than 12%. This indicated that the model was also able to predict the effect of thermal pretreatment on the increase of ammonium in the effluent.

In overall, it can be observed in Fig. 6.5.3 that the differences in operation conditions for each digester, regarding the application of pretreatment and reduction of HRT, were correctly represented by the model. Increases in the values mainly of the disintegration coefficients of the ADM1, as well as the solubilization of COD promoted by the thermal pretreatment, coupled to the increased flow rate applied to the model (for digester B only) were assumed to be responsible for those distinct behaviors. The changes in CH_4 production levels are evident when comparing digester A (Fig. 6.5.3a) and C (Fig. 6.5.3c), and even more when considering the high CH_4 production of digester B (Fig. 6.5.3b), and the simulations were able to follow closely those tendencies. In respect to the accuracy of the model considering the average CH_4 production, Table 6.5.4 shows the high quality of the predictions in both phases, with average overestimations (or underestimations) lower than 15%, and as low as 1.1%. This clearly demonstrates that the procedures and considerations used to perform the simulations with the calibrated model were successful in predicting the behavior of the three digesters.

Table 6.5.4. Comparison between experimental and simulated average methane production for the three digesters in phases II and III, as well as model's overestimation in each case.

	Phase II			Phase III		
	A	B	C	A	B	C
Experimental CH_4 production ($L.d^{-1}$)	104 ± 17	162 ± 29	89 ± 20	120 ± 25	219 ± 57	117 ± 17
Simulated CH_4 production ($L.d^{-1}$)	119 ± 14	185 ± 36	90 ± 16	134 ± 29	233 ± 58	101 ± 18
Overestimation (%)	14.4	14.2	1.1	11.7	6.4	-13.7[a]

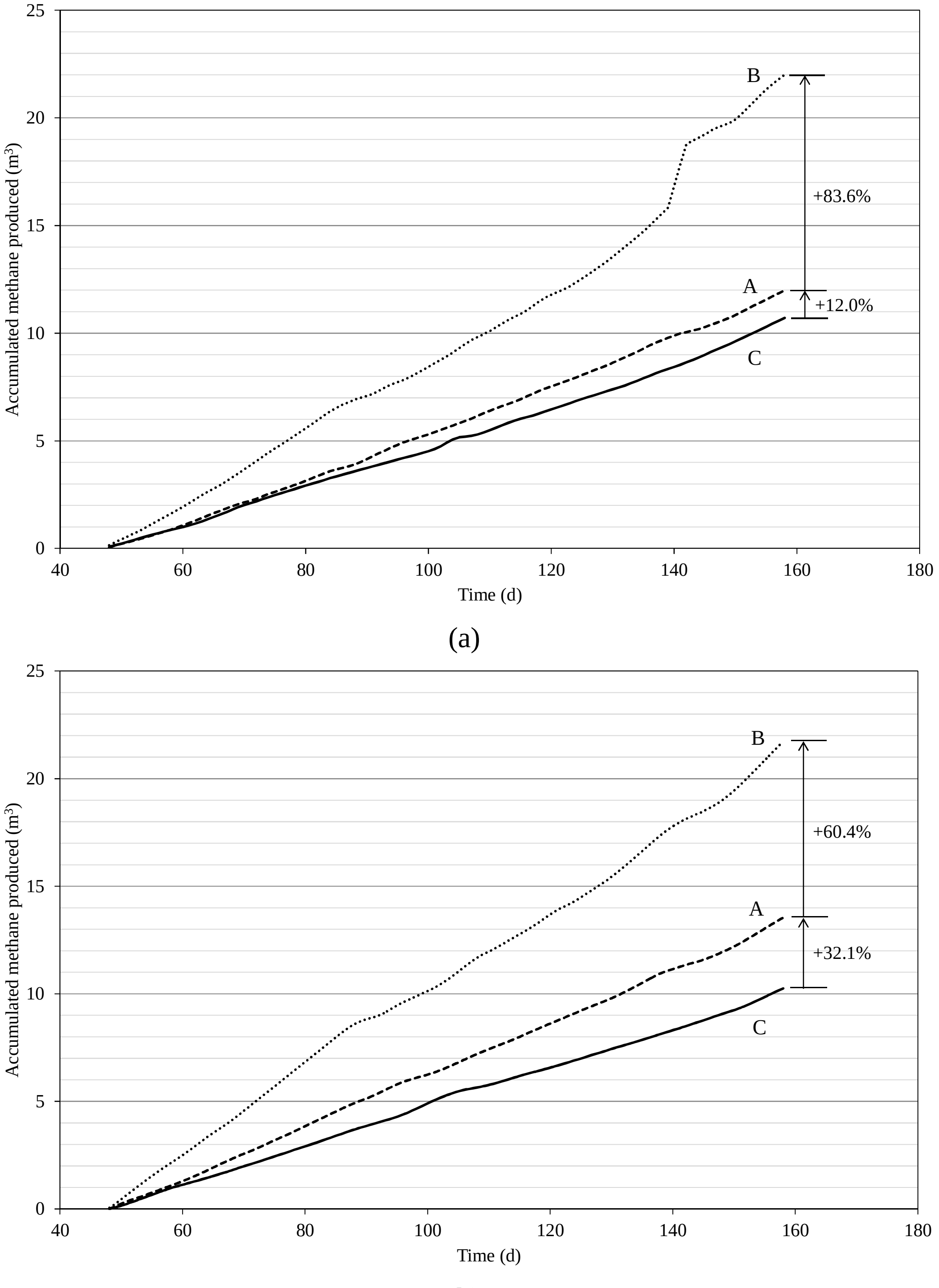
[a] Negative values means that the simulation underestimated the parameter.

3.4 Thermal pretreatment and HRT assessment

The effect of the thermal pretreatment and changes in HRT on the performance of digesters A, B and C were assessed using the accumulated CH_4 production curves throughout the whole operation period (not considering phase I), as shown in Fig. 6.5.4, both for experimental data and simulation results. This was done to account for the global differences between each digester, regardless of punctual variations of CH_4 production, and a similar approach was also reported by Phothilangka et al. (2008).

It can be observed in Fig. 6.5.4a that the global accumulated CH_4 production of digester A suffered a small increase of only 12%, when compared to the control digester (C). As also discussed in section 3.1, this improvement is lower than expected, since other studies obtained increases in CH_4 production of 20-30% when treating mixed sludge (Barjenbruch and Kopplow, 2003; Pérez-Elvira and Fdz-Polanco, 2012), although there are reports of lower increases in the range of 10-20% (Haug et al., 1978; Donoso-Bravo et al., 2011b), which depend on experimental conditions, variability of results and performance of digesters in each case. The improvement in CH_4 production for digester A was more optimistic according to simulation results (Fig. 6.5.4b), accounting for an enhancement of 32.1% when compared to digester C, since overestimation was evident in some operation periods, such as the one depicted in region (a1) (Fig. 6.5.3a).

When the accumulated CH_4 production of digester B is compared with digester A, increases in this parameter were 83.6% and 60.4%, for experimental data and simulation results, respectively (Fig. 6.5.4). Those differences were affected by the results of digester A, discussed above. Nonetheless, when digester B is compared with the control, differences in CH_4 accumulation were accurately represented by the simulations, accounting for an enhancement of 95.6 and 92.5%, for experimental data and simulations results, respectively. These results show that reducing the HRT from 20 to 10 days had a great effect on CH_4 production, and digester B could sustain such an increase in organic load throughout the operation period. Although the flow rate is doubled in this case, CH_4 production does not double as well, due to the fact that the anaerobic digestion process is limited under such HRT and organic load, and the specific CH_4 yield ($L.(gVS_{fed})^{-1}$) is reduced. In this context, Pérez-Elvira and Fdz-Polanco (2012) obtained an increase in biogas production of 71.4% when reducing the HRT from 17 to 9 days in digesters fed with a substrate similar to S1, with a coupled decrease in the specific biogas yield from 652 to 607 $L.(gVS_{fed})^{-1}$. The reported increase in biogas production is similar to both the experimental (83.6%) and simulated (60.4%) increases in CH_4 production when comparing digesters A and B.



(a)

(b)

Figure 6.5.4. Experimental (a) and simulated (b) methane accumulated throughout the operation period (not considering phase I) for digesters A (---), B (···) and C (–). Upward arrows represent the improvement in methane production between each pair of digesters.

Considering the final amount of CH_4 produced in each digester, Table 6.5.5 shows that the model presented extremely high accuracy for digesters B and C, with a slight underestimation of the accumulated CH_4. Simulations related to digester A, however, presented less quality in this regard, with an overestimation of 13.4%. Nevertheless, those are acceptable levels of accuracy taking into account the variability of operation. Therefore, results demonstrate the feasibility and usefulness of using the ADM1 under the studied conditions to predict the effects of both a thermal hydrolysis pretreatment and the manipulation of HRT in the operation of sludge digesters.

Table 6.5.5. Comparison between experimental and simulated total methane accumulation throughout operation in phases II and III for each digester, and overestimation of the predictions.

	A	B	C
Experimental CH_4 accumulation (m^3)	11.9	22.0	10.7
Simulated CH_4 accumulation (m^3)	13.5	21.7	10.2
Overestimation (%)	13.4	-1.4	-4.7

[a]Negative values mean that the simulation underestimated the parameter.

4 CONCLUSIONS

The results provided by the present study demonstrated the feasibility and usefulness of using the ADM1 to predict and assess the effects of both thermal pretreatment and changes in HRT in the performance of sewage sludge digesters. The calibration results, obtained via BMP assays, showed an important increase in the disintegration step, caused by the pretreatment, and the validation of the calibrated model presented good accuracy even considering operational variability, with under/overestimation of both average and accumulated CH_4 production lower than 15% in all cases.

Acknowledgements

This research group is “Grupo de Excelencia GR76 de la Junta de Castilla y León” and member of the Consolider_Novedar framework (Project CSD2007-00055, Programa Ingenio 2010, Spanish Ministry of Education and Science). The experimental data of CTH were obtained within the project SostCO2 led by Aguas de Barcelona (Aqualogy). The authors would like to thank Guzmán Garcia for his contribution.

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Capítulo 7

Conclusiones y evaluación energética

Es obligado relacionar las conclusiones que se extraen el término de la tesis con el objetivo planteado inicialmente, recogido en el Capítulo 4: “**OPTIMIZACIÓN DE LA DIGESTIÓN ANAEROBIA DE DISTINTOS RESIDUOS ORGÁNICOS INDUSTRIALES, AGRÍCOLAS, GANADEROS Y URBANOS MEDIANTE LA INTRODUCCIÓN DE UN PRE-TRATAMIENTO DE HIDRÓLISIS TÉRMICA CON EXPLOSIÓN DE VAPOR”**.

Como **parámetro de evaluación** se tomó el factor de biodegradabilidad, definido como la producción de metano del residuo hidrolizado térmicamente con respecto al residuo no tratado. El ajuste de los resultados de los ensayos de potencial metanogénico mediante ecuaciones de primer orden permitió completar los resultados de productividad con parámetros relativos a las cinéticas de degradación.

Las **condiciones de operación** a optimizar fueran temperatura y tiempo de hidrólisis, cuya combinación fue aunada en el factor de severidad, que ha sido el parámetro manejado a lo largo de la tesis. La evaluación de la influencia de ambos parámetros se realizó mediante la metodología de superficie de respuesta o análisis de varianza, con el objetivo de determinar qué parámetro presenta mayor influencia.

La **primera conclusión** clara que se ha obtenido trabajando con distintos residuos es que la hidrólisis térmica no consigue mejorar la biodegradabilidad de cualquier residuo orgánico. Por tanto, antes de plantear la implementación de un pre-tratamiento de hidrólisis (térmico o de cualquier naturaleza), es necesario un estudio previo que confirme si el tratamiento conduce a un aumento de la productividad y/o a una mejora de la cinética de degradación.

La **segunda conclusión** es relativa a las condiciones de pre-tratamiento: El óptimo resultante de la combinación de temperatura-tiempo de hidrólisis no coincide para todos los residuos, y por ello es igualmente necesario realizar una optimización específica para cada uno.

A continuación se resume **para cada uno de los cinco residuos ensayados**, las principales **conclusiones** obtenidas en las condiciones ensayadas:

Bagazo de cerveza

- Las condiciones ensayadas (150-220ºC y 1-15 minutos), correspondientes a factores de severidad en el rango 1.5-4.7, han mostrado que el tratamiento térmico no conduce a una mejora en la biodegradabilidad del bagazo de cerveza.
- Para factores de severidad superiores a 3.5 las productividades obtenidas fueron inferiores a la correspondiente al bagazo no tratado (360 mL CH_4/g SV_{alim}).

Cáscara de naranja

- Las condiciones ensayadas (170-190ºC y 7-30 minutos), correspondientes a factores de severidad en el rango 2.9-4.2, han mostrado que el tratamiento térmico no conduce a una mejora en la biodegradabilidad de la cáscara de naranja.
- Las productividades obtenidas fueron siempre inferiores a la correspondiente a la cáscara de naranja no tratada (236 mL CH_4/g SV_{alim}), y menores cuanto mayor fue la severidad del tratamiento.
- Este empeoramiento podría deberse a la formación o liberación de compuestos inhibitorios o recalcitrantes, como el D-limoneno, reconocido inhibidor de las bacterias anaerobias.

Paja de trigo

- Las condiciones ensayadas (150-220ºC y 1-15 minutos), correspondientes a factores de severidad en el rango 1.5-4.3, han mostrado que no todo tratamiento térmico conduce a una mejora en la biodegradabilidad de la paja de trigo.
- El óptimo de productividad se obtuvo en torno al factor de severidad de 3.5, correspondiente a las condiciones de operación de 200ºC-5min y 220ºC-1min.
- En dichas condiciones óptimas, la productividad aumentó del orden de un 20-25% (de 230 a 290 mL CH_4/g SV_{alim}).
- Igualmente, la velocidad de degradación prácticamente se duplicó (de 15 a 28 mL CH_4/g SV.d).
- El estudio cinético realizado mostró que la hidrólisis resulta limitante, aumentando el valor de la constante de hidrólisis en los ensayos con paja tratada.
- El estudio de la influencia de parámetros tales como el tamaño de partícula o la adición de agua (de gran interés desde el punto de vista de la operación a escala real) mostraron que la inversión económica en molienda y en dilución no favorecen los resultados finales de productividad.

Purines de cerdo

- Las condiciones ensayadas (120-180ºC y 5-60 minutos), correspondientes a factores de severidad en el rango 1.3-4, han mostrado que todo tratamiento térmico conduce a una mejora en la biodegradabilidad del purín de cerdo.
- El óptimo de productividad se obtuvo en torno al factor de severidad de 3.5-4, correspondiente a las condiciones de operación de 170ºC-15min, 170ºC-30min, 180ºC-5min.
- En dichas condiciones óptimas, la productividad aumentó del orden de un 200% (de 160 a 310-320 mL CH_4/g SV_{alim}).
- La velocidad de degradación para el purín pre-tratado fue más de dos a tres veces mayor (de 32 a 70-100 mL CH_4/g SV.d).

Lodos de depuradora

- La única condición ensayada (170ºC y 40 minutos), correspondiente a un factor de severidad de 3.7, ha conducido a un incremento en la productividad de metano de aproximadamente un 20%. Se debe tener en cuenta que el tratamiento se realizó únicamente a lodo secundario, y la digestión se realizó a lodo mixto.
- Las condiciones de operación se han fijado tomando como referencia estudios previos.
- El *Anaerobic Digestion Model Nº1* (ADM1), calibrado mediante los resultados obtenidos en ensayos BMP, ha demostrado ser una buena herramienta para simular y predecir el comportamiento de digestores operados en continuo.

Finalmente, resulta interesante resumir que de los cinco residuos ensayados, sólo en tres de ellos (paja, purín y lodos de EDAR) la hidrólisis térmica ha conducido a una mejora en la biodegradabilidad del residuo. En concreto, el mayor aumento en productividad ha correspondido al purín de cerdo, en que se ha duplicado, mientras que para la paja y el lodo el incremento obtenido corresponde a un 20-30%.

Con respecto a las condiciones de operación, los tres residuos han mostrado un óptimo en factor de severidad en torno a 3.5, si bien la combinación temperatura-tiempo óptima ha sido diferente:

- Paja de trigo: 200ºC y 5 min
- Purín de cerdo y lodos: 170ºC y 15-30 min

A continuación se realiza una breve reflexión sobre aspectos energéticos a partir de las conclusiones experimentales extraídas en materia de condiciones de operación.

Evaluación energética

Aunque no es el objetivo de la tesis, a partir de los resultados obtenidos se ha planteado una **evaluación energética** que muestre si el tratamiento de hidrólisis térmica investigado presenta un interés económico, o si por el contrario el balance energético resulta absolutamente negativo, y por tanto de nula aplicabilidad real.

Las **bases** sobre las que se debe asentar una evaluación energética a un proceso de este tipo son:

1- Características de la alimentación, siendo fundamental el parámetro de concentración, dado que la cantidad de agua contenida en el residuo está directamente relacionada con el desperdicio térmico en calentar dicho agua, y no en la propia hidrólisis.

2- La integración energética en la unidad de hidrólisis y entre la unidad de pre-tratamiento y la de digestión es crucial (se amplia esta idea en los siguientes puntos 3 y 4).

3- En una unidad de hidrólisis térmica bien diseñada, el vapor generado en el flash se emplea para precalentar la alimentación al reactor de hidrólisis hasta 100ºC, de modo que la energía requerida para operar el sistema corresponde al calentamiento desde 100ºC hasta la temperatura de operación (ejemplo: 170ºC para lodos y purines, y 200ºC para paja).

4- Esta energía térmica necesaria se debe obtener a partir del biogás generado, siendo la opción prioritaria el empleo de un ciclo combinado, en que se obtenga energía eléctrica y el calor residual de los gases de escape sea suficiente para generar el vapor necesario en el pre-tratamiento térmico. La alternativa de quemar biogás en una caldera carece de interés económico, al perderse la capacidad de generar “energía verde”.

La Figura 7.1 muestra el esquema propuesto.

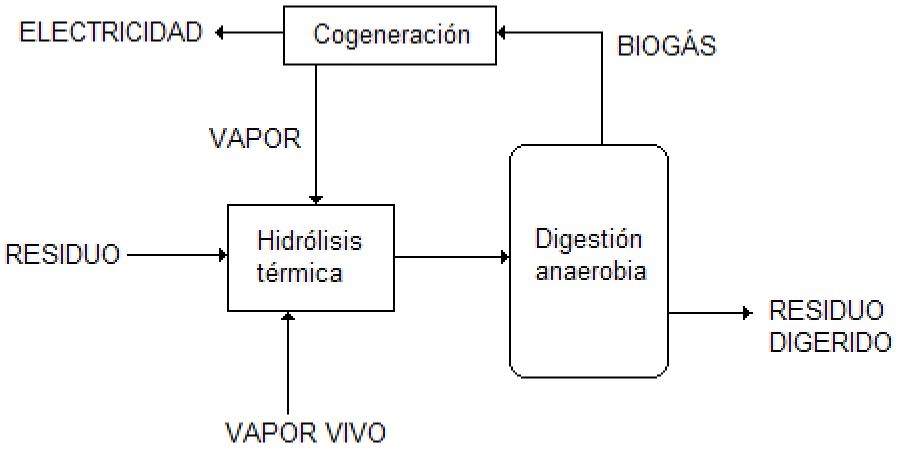

Figura 7.1. - Esquema de integración energética propuesto

La **configuración ideal** correspondería a las condiciones de operación que permitan operar con un aporte nulo de vapor vivo, obteniéndose sin embargo un incremento en la generación de biogás (energía) y un descenso en la cantidad de residuo resultante.

Como se ha indicado anteriormente, en este sentido la <u>concentración</u> de la alimentación juega un papel fundamental desde el punto de vista de minimizar la energía térmica requerida para el pre-tratamiento, y maximizar la carga de digestión, y por tanto de generación de biogás, y consiguiente energías eléctrica y térmica.

El balance energético correspondiente al tratamiento de lodos de depuradora se encuentra ampliamente descrito en la referencia correspondiente a Pérez-Elvira S.I. & Fdz-Polanco F. (2012), que concluye afirmando que la integración buscada se logra operando la hidrólisis de lodo secundario a una concentración de 13%ST, y posterior digestión de lodo mixto.

Se ha realizado un balance similar a los residuos paja de trigo y purines de cerdo con el objetivo de comparar la **energía térmica requerida para el pre-tratamiento** (ETR) y la **energía térmica generada en el ciclo combinado** (ETG). Las ecuaciones 7.1 y 7.2 muestran respectivamente el modo en que se han calculado ambas.

$$ETR\ (kj/kg_{residuo}) = C_p * \Delta T \qquad (7.1)$$

donde:

Cp (kJ/kg.ºC): capacidad calorífica

ΔT (ºC): diferencia entre la temperatura de operación en el reactor de pre-tratamiento (170ºC, 200ºC, 220ºC) y la alcanzada durante el precalentamiento (100ºC)

$$ETG\ (kJ/kg_{residuo}) = 0.9 * 0.33 * P_{TH} * SV * \Delta H_{comb.CH_4} \qquad (7.2)$$

donde:

0.9: eficacia supuesta al cambiador de calor que genera vapor a partir de los gases de escape

0.33: suposición de que aproximadamente 1/3 de la energía generada en el ciclo combinado es evacuada como gases de escape

P_{TH} (NL CH_4/kg $SV_{alimentado}$): productividad de metano obtenida para el residuo tratado térmicamente

SV (g SV/kg): concentración de sólidos volátiles en el residuo de alimentación

$\Delta H_{comb\ CH_4}$ (kJ/NL CH_4): entalpía de combustión del metano (35.8 kJ/NL CH_4)

La Tabla 7.1 recoge los valores de caracterización y productividad manejados experimentalmente, y los residuos obtenidos para las energías requerida (ETR) y generada (ETG).

	Paja de trigo	**Purín de cerdo**
Cp (kJ/kg.ºC):	1.63	3.52
SV (g SV/kg)	0.850	0.140
ΔT (ºC)	100	70
P_{TH} (NL CH_4/kg $SV_{alimentado}$)	270	329
ETR (kJ/$kg_{residuo}$)	163	246
ETG (kJ/$kg_{residuo}$)	2437	490

Tabla 7.1. - Resultados del balance de energía realizado a paja de trigo y purín de cerdo

Los valores obtenidos muestran un **balance energético positivo** en ambos, siendo el caso de la paja extremadamente positivo.
La justificación de este hecho es clara: la gran sequedad de la paja (<10% de humedad) conduce a un valor muy elevado de generación de energía por unidad de residuo.

Este factor, unido a la capacidad de incremento de carga en los digestores obtenida en la experimentación realizada en los ensayos de BMP (mejora en la cinética) conducen a que **resulte de gran interés plantear el co-tratamiento de distintos residuos**, de modo que aquellos más concentrados (i.e.: paja de trigo) garanticen el balance energético de aquellos de mayor contenido en agua (lodos, purines,…).

Desde un punto de vista más global, un balance energético completo debería considerar otros aspectos tales como el calentamiento del digestor para asegurar la operación mesófila deseada. La introducción de un pre-tratamiento de hidrólisis térmica y la consiguiente posibilidad de operación de digestores a mayor carga de la convencional que incremente la generación de biogás apuntan a que el proceso global resulte ventajoso frente al convencional, si bien es preciso realizar los cálculos específicos al caso concreto de implementación que se considere.

Capítulo 8

Líneas Futuras

Como se ha resumido en las conclusiones, el estudio individual realizado a los distintos residuos ha dado lugar a un rango de condiciones óptimas (coincidentes o no entre ellos) y a unas perspectivas positivas desde el punto de vista energético.

Si bien el estudio de laboratorio ha sido riguroso, considerando como norte una posible aplicabilidad práctica, existen una serie de cuestiones que deberían ser observadas, y que se exponen a continuación como propuesta de líneas futuras de trabajo:

1 - La primera es el paso a **operación de digestores piloto en continuo**, alimentados con el/los residuos sometidos a pre-tratamiento térmico. De este modo, se pueden garantizar y chequear tanto las condiciones óptimas de pre-tratamiento como los temas de reología y mezcla, posibles inhibiciones, cargas de trabajo, etc.

2 - Tanto por las coincidentes condiciones óptimas de hidrólisis térmica experimentadas para algunos residuos, como por el interés energético que supone el pre-tratamiento térmico de corrientes de elevada concentración, hay un campo muy interesante de trabajo en **co-pretratamiento** y en **co-digestión de distintos residuos**, con el objetivo de optimizar la economía global del tratamiento de los distintos residuos.

3 - Finalmente, las propuestas 1 y 2 se deben completar con una **evaluación energética** apoyada en una o varias situaciones concretas de flujos de alimentación, consumos energéticos en pre-tratamiento y digestión, y productividades finales de biogás que permitan hacer un balance energético global que compare el incremento en el consumo energético al introducir un pre-tratamiento térmico frente al beneficio energético derivado del incremento en biogás.

Capítulo 9

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Capítulo 10

Anexos

Bioresource Technology 143 (2013) 251–257

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Influence of thermal pretreatment on the biochemical methane potential of wheat straw

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HIGHLIGHTS

- Influence of thermal pretreatment on the anaerobic biodegradation of wheat straw.
- Evaluation through BMP tests and modeling.
- Optimum severity factor at 220 °C and 1 min (3.5 severity factor).
- First order model confirmed that the hydrolysis is the limiting step.
- Surface response evaluation indicated negligible interaction temperature–time.

ARTICLE INFO

Article history:
Received 25 February 2013
Received in revised form 15 May 2013
Accepted 17 May 2013
Available online 23 May 2013

Keywords:
Biochemical methane potential
Thermal hydrolysis
Pre-treatment
Mathematical modeling
Wheat straw

ABSTRACT

The biochemical methane potential of steam exploded wheat straw was evaluated in a pilot plant under different temperature–time combinations. The optimum was obtained for 1 min and 220 °C thermal pretreatment (3.5 severity factor), resulting in a 20% increase in methane production respect non-treated straw. For more severe treatments the biodegradability decreased due to a possible formation of inhibitory compounds. The results of the tests were modeled with a first order equation to estimate the hydrolysis constant and biodegradability extent, and the influence of temperature and time on the kinetic parameters was obtained with a response surface study. The data processing confirmed the accuracy of the model and the optimum operation conditions, and demonstrated that the biomethanization of raw and pretreated wheat straw is limited by the hydrolysis, being the individual influence of temperature and time much more important than the interaction between them.

1. Introduction

In many countries, lignocellulosic materials are an abundant agricultural residue which can be used either for animal feeding or for energetic valorization in power plants. In Europe, wheat straw represents the largest agricultural waste, being in Spain an important part of the crop wastes which could be used as biomass for renewable energy production. The use of renewable energy sources is becoming increasingly necessary in order to cope with the impacts of global warming. The conversion of biomass into energy can be achieved in a number of ways, being anaerobic digestion a very sustainable alternative.

Anaerobic digestion is a well-known process for the treatment of wastewater of organic wastes. This process presents advantages over some conventional aerobic technologies, such as the better handling of wet waste, the production of biogas as a renewable source of energy and the attenuation of odor problems (Palmowski and Muller, 2000; Pérez-Elvira et al., 2011, 2010). Furthermore, anaerobic digestion is the most cost-effective treatment, due to high energy recovery and low environmental impact (Mata-Alvarez et al., 2000). However, the application of anaerobic digestion with lignocellulosic biomass has not been a subject of enough research.

Lignocellulosic material is mainly composed of three different types of polymers: cellulose, hemicellulose and lignin. While cellulose has a rigid and crystalline form, hemicellulose has a lower molecular weight and short lateral chains, which corresponds to an easy hydrolysable polymer. The third compound, lignin, is one of the most abundant polymers in nature. It is a complex and amorphous heteropolymer consisting of three different phenylpropane units, and is also non-water soluble (Hendriks and Zeeman, 2009). Wheat straw consists mainly of cellulose (30–40%), hemicellulose (20–30%) and lignin (10–20%). The cellulose and hemicellulose

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http://dx.doi.org/10.1016/j.biortech.2013.05.065

fractions can be enzymatically hydrolyzed to monomeric sugars after a pre-treatment aiming to hydrolyze its partially crystalline structure (Puls and Schuseil, 1993).

The hydrolysis of this type of biomass is limited by several factors, such as the lignin content. In cellulose the molecules are linear, and therefore they can form hydrogen bonds between the chains that limit their solubility in water, and reduce the available surface area, making cellulose difficult to degrade. A number of pretreatments for ligmocellulosic biomass are currently available, such as mechanical, milling into smaller pieces (Mshandete et al., 2006; Palmowski and Muller, 2000), physico-chemical such as dilute alkaline pretreatment (McIntosh and Vancov, 2011) or dilute acid pretreatment (Schell et al., 2003), wet oxidation, thermal treatment (Sapci, 2013), or a combination of them (Linde et al., 2008; Nkemka and Murto, 2013). From the point of view of its applicability, the total energy balance of the global process (considering both pre-treatment and digestion) must be taken into consideration. Compared to other pretreatment methods, the thermal hydrolysis can be cost effective if a proper steam-explosion and energy recovery is performed. The warranty that the process is energetically self-sufficient is described in Pérez-Elvira and Fdz-Polanco (2012). Furthermore, hydrothermal treatment can be performed without addition of chemicals or oxygen, representing a potential solution for the pretreatment of large quantities of lignocellulosic biomass including woods material (Horn et al., 2011a; Sipos et al., 2010) and agricultural by-products (Horn et al., 2011b; Ohgren et al., 2006).

Thermal pretreatment is a method where the substrates are subjected to heating under a specific pressure during a certain period of time. At the end of the heating, a steam explosion occurs, where the biomass is rapidly discharged into normal pressure causing an explosion of the macromolecules. At temperatures in the range 150–180 °C, parts of lignocellulosic materials will start to solubilize (Garrote et al., 1999). Some studies have shown that the effect of the thermal treatment depends on several factors, such as: residence time, operating temperature, chip size, and moisture content (Bauer et al., 2009; Han et al., 2010; Zhang et al., 2008). A too harsh treatment of lignocellulosic biomass may result in a lower methane yield and longer retention time. The reason is that when lignin is broken, there is a risk of formation phenolic and hererocyclic compounds from hemicellulose and cellulose degradation, like furfural and hydroxymethylfurfural (HMF), which are known to inhibit many fermented microorganisms, including those involved in the biogas generation (Hendriks and Zeeman, 2009). According to Raj (2009) the concentration of furfural that inhibits methanogens ranges from 2400 to 3000 mg/L.

The aim of this research is to study the impact of thermal hydrolysis on the biodegradability of wheat straw under mesophilic anaerobic conditions, by using an experimental approach and mathematical modeling of the results. The final applicable objective is to define the pretreatment parameters that optimize the methane productivity.

2. Methods

2.1. Raw material

Wheat straw was grown in Valladolid (Spain) and harvested in 2011. For all the experiments, the straw was cut into pieces of 10 cm long. The average values obtained in wheat straw characterization are: 922 ± 2 g TS/kg (92%VS/TS), 1078 ± 8 g TCOD/kg, 4.72 g N-TKN/kg, and a ratio C/N around 92.

2.2. Thermal pre-treatment pilot plant and operation conditions

The Cambi® thermal treatment plant, steam explosion unit, consists of a 30 L reactor and a flash tank with a removable bucket to collect the pretreated material (Fig. 1). The steam is generated by a 25 kW electric steam boiler (200 L capacity) which can supply steam up to a maximum pressure of 34 bar (240 °C). Wheat straw is loaded into de reactor using a motorized (M) ball valve (V4) at the top of the reactor. Steam is added to the reactor from the bottom, through an air-actuated valve (V1), heating the waste during the time established. The desired operation pressure (corresponding to a certain temperature) is set on the control panel unit, controlled automatically by the air-actuated valve (V1). For security reasons also a manual valve (V2) has to be opened to add steam to the pressure reactor. An air-actuated ball valve at the bottom of the vessel (V3) is responsible for the rapid pressure drop (explosion) and release of the pretreated biomass to the flash tank. The pretreated biomass is collected in a removable bucket at the bottom of the flash tank. The steam that is leaving the flash tank is condensed and led to a water tank (WT). Any steam that is not condensed leaves the unit via a carbon filter (CF) to remove smell.

Different pre-treatment conditions were tested varying both temperature (ranging 150–220 °C) and time (ranging 1–15 min). In all the experiments, one kilogram of wheat straw was used. The reactor was preheated for about 15 min at the same temperature selected for the pre-treatment before starting the experiments.

Temperature and time determine the severity factor of the treatment. This parameter ($\log R_0$, Eq. (1)) is most widely accepted for steam pre-treatments (Hendriks and Zeeman, 2009) to express the severity of the pre-treatment:

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \tag{1}$$

where t is the time (min), T the temperature (°C), 100 is the base temperature (100 °C), and 14.75 is the activation energy based on the assumption that the reaction is hydrolytic and the overall conversion is first order (Xu et al., 2011). This expression only takes into account time and temperature, and does not consider the effect of the flash. The study of this effect is not assessed in this paper.

Theoretically, the more severe a treatment is, the more cellulose is made available for digestion. However, very severe pre-treatments can lead to formation of inhibitory compounds from the macromolecules, driving to an indirect relationship between the severity factor and the biodegradability. Therefore there should be an optimum value for the severity factor.

2.3. Anaerobic biodegradability

Batch anaerobic digestion tests (BMP) were carried out in triplicate to assess the wheat straw biodegradability after the different pre-treatment conditions applied. A control test without substrate and a control with cellulose were included in order to check the methanogenic activity of the inoculum. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1 ± 0.3 °C), with constant mixing in a rotary desk.

The anaerobic inoculum used for the batch test was taken from a pilot-scale mesophilic anaerobic digester treating mixed sludge from a municipal wastewater treatment plant, with a volatile solids (VS) concentration of 12 gVS/kg. The inoculum was pre-incubated for four days (35.1 ± 0.3 °C) in order to minimize its residual biodegradable organic material content.

Bottles of 2 L volume were used, made of borosilicate glass (260 mm height, 160 mm diameter and a 40 mm bottleneck), placed horizontally in a rotary table to achieve a good mixing.

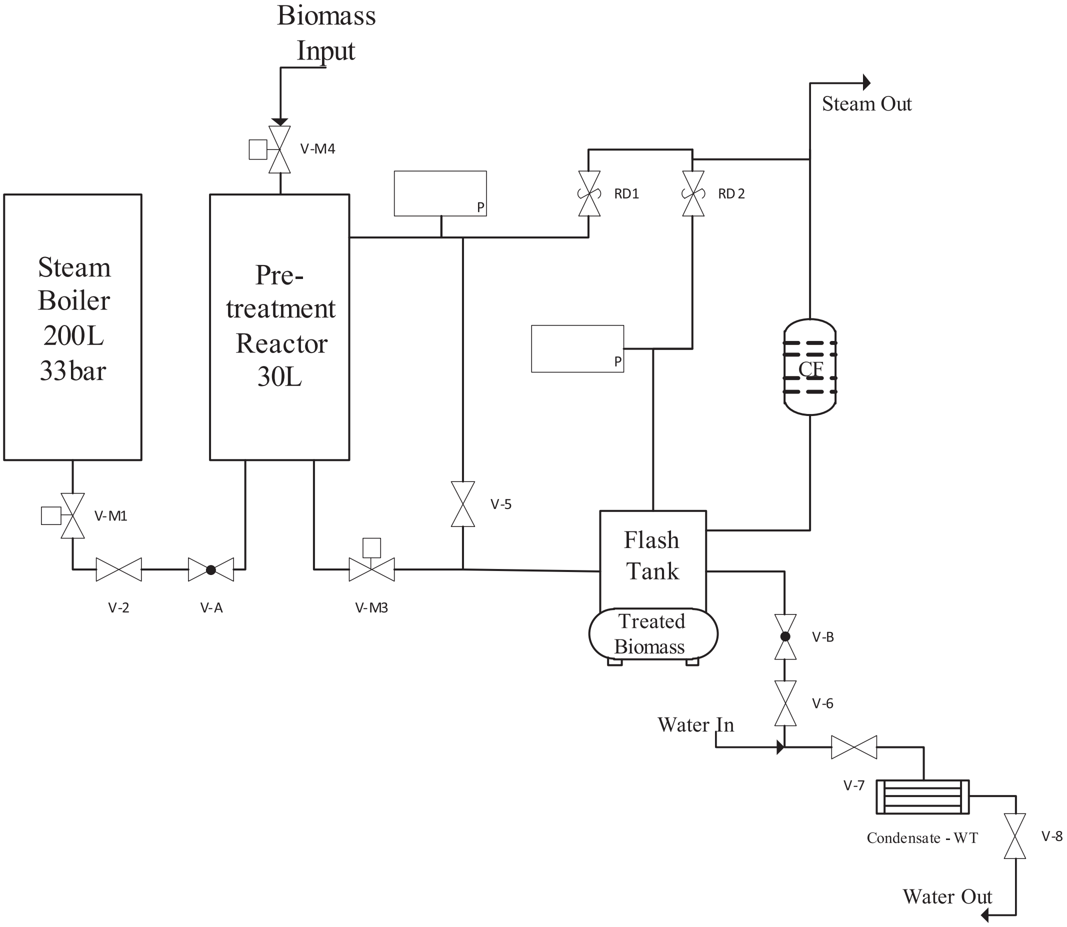

Fig. 1. Cambi® steam explosion unit. V – valves; VM – motorized valves; VA,B – one way valves; P – manometers to measure pressure; RD – safety valves; CF – carbon filter; TB-T – treated biomass tank; WT – water tank.

The liquid volume was 400 mL in order to have enough headspace, and the substrate/inoculum (S/I) ratio selected was 0.5 gVS/gVS as suggested by Neves et al., 2004 and Angelidaki et al., 2009.

Biogas production was measured manually by a pressure transmitter (ifm, PN5007, range 1 bar) in the head space of each reactor and the biogas composition was measured by gas chromatography (Varian CP-3800 CG TCD). The biogas production was followed for about 40 days. All values of specific methane yield (mL CH_4/gVS_{fed}) are presented under standard temperature and pressure conditions (STP – 0 °C, 1 atm) defined by IUPAC (International Union of Pure Applied Chemistry), and divided by the mass of volatile solids of substrate fed into the assay.

Theoretical methane yield (Nm^3 CH_4/kg VS) was calculated from the characterization performed to the wheat straw as follows:350 mL CH_4/g $TCOD_{removed}$ × 1.27 g TCOD/g VS = 444 mL CH_4/g $VS_{removed}$.

This value is in agreement with the one calculated by Kaparaju et al. (2009) considering the stoichiometric conversion of the organic matter (426 mL CH_4/g $VS_{removed}$).

2.4. Analytical method

Substrates, inoculum and digestates were characterized in all the experiments. Total and volatile solids (TS and VS) and total Kjeldahl nitrogen (TKN) were measured following the procedures given in Standard Methods for Examination of Water and Wastewater (APHA et al., 2005). Total chemical oxygen demand (TCOD) was determined according to standard UNE 77004:2002 based in dichromate method. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

Table 1
Conditions applied for the different experiments performed.

Experiments	Ref.	P (bar)	T (°C)	Time (min)	log R_0	mLCH_4/g VS_{fed}	FN
Untreated	0	–	–	–	–	226 ± 11	–
TH-1	1	5	150	15	2.65	185 ± 28	0.82
TH-2	2	8	170	5	2.76	159 ± 16	0.70
TH-3	3	8	170	15	3.24	250 ± 19	1.10
TH-4	4	16	200	2	3.25	211 ± 22	0.93
TH-5	5	16	200	5	3.64	238 ± 18	1.05
TH-6	6	16	200	15	4.12	202 ± 2	0.89
TH-7	7	23	220	1	3.53	273 ± 3	1.21
TH-8	8	23	220	5	4.23	214 ± 28	0.95

2.5. Parameters determination and evaluation methodology

2.5.1. Parameters determination from BMP test

When the hydrolysis reaction is the rate-limiting step of the global process, as happens in the anaerobic degradation of lignocellulosic substrates, the first order model (Eq. (2)) is commonly used to estimate the reaction extent B_0 (related to the substrate

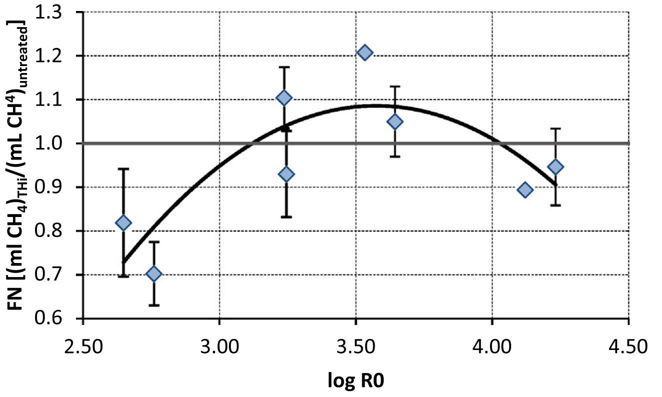

Fig. 2. Normalized methane productivity (FN [(mL CH_4)$_{THi}$/(mL CH_4)$_{untreated}$]) with respect to the severity factor (log R_0).

biodegradability) and the hydrolysis constant k_h, which both could be used in a global model of the anaerobic digestion process (such as ADM1) to predict the performance of the anaerobic digester (Batstone et al., 2009; Donoso-Bravo et al., 2010; Ge et al., 2011).

$$B = B_0 \cdot (1 - \exp(-K_h \cdot t)) \qquad (2)$$

where B is the biogas production (ml/gVS$_{fed}$)

2.5.2. Model accuracy determination

Apart from obtaining the best combination of parameters, it is even more important to know the accuracy of the estimated values. The Fisher matrix (FIM) summarizes the quantity and quality of the information obtained in the experiment and, assuming proper model selection with no data autocorrelation and uncorrelated error, the inverse of the FIM (Eq. (3)) corresponds to the parameter estimation covariance matrix (C_j).

$$C_J = (F(\theta))^{-1} \quad \text{where} \quad F(\theta) = \sum_{i=1}^{N} \left[\frac{\partial y_i(t,\theta)}{\partial \theta}\right]^{\mathrm{T}} Q_i^{-1} \left[\frac{\partial y_i(t,\theta)}{\partial \theta}\right] \qquad (3)$$

Finally, once the covariance matrix is available, an approximation of the standard deviation of the parameters can be estimated through Eq. (4).

$$\sigma(\theta_i) = \sqrt{C_J} \qquad (4)$$

2.5.3. Response surface methodology (RSM)

This methodology allows evaluating the combined effect of several variables (temperature and time in this case) and the interaction between them on a specific response (in this case, those parameters obtained in Section 2.5.2). The polynomial shown in Eq. (5) considers the effect of both variables as well as the combined influence of them. The coefficients of the equation were obtained by minimizing the least square function, and determination coefficient was calculated to know the fraction of the variability of the data that is explained by the model. The analysis was carried out in Matlab®.

$$Y = p_1 + p_2 x_1 + p_3 x_2 + p_4 x_1 x_2 \qquad (5)$$

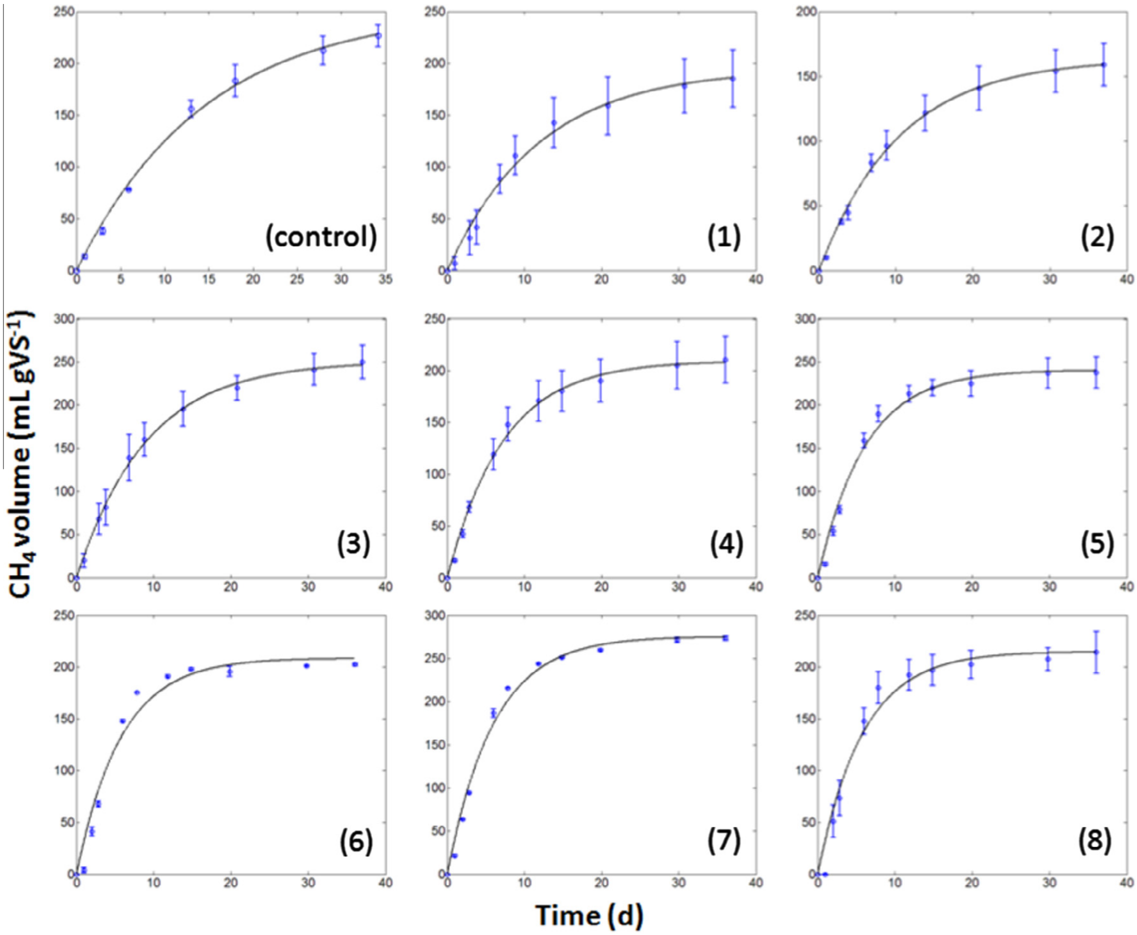

Fig. 3. First order model fit. Experimental information (blue points), model profile (black solid line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Results of the parameters determination.

Exp.	T (°C)	t (min)	First order model				
			B_0		k_h		R^2
			mean	SD[a]	mean	SD[a]	
0	0	0	252.1	9.2	0.069	0.006	0.997
1	150	15	194.6	8.2	0.085	0.009	0.989
2	170	5	163.4	3.0	0.097	0.005	0.997
3	170	15	250.6	3.6	0.110	0.004	0.998
4	200	2	209.2	4.0	0.138	0.008	0.995
5	200	5	240.7	6.8	0.164	0.015	0.987
6	200	15	208.6	9.3	0.175	0.025	0.968
7	220	1	275.5	6.9	0.168	0.014	0.989
8	220	5	214.9	8.7	0.173	0.023	0.973

[a] SD: standard deviation.

where Y is the variable response, x_1 is the pretreatment time, x_2 is the pretreatment temperature, and $p_1 ... p_4$ are the regression coefficients of the model.

3. Results and discussion

3.1. Pre-treatment experimental study

The temperature–time combinations selected for the study are presented in Table 1. For each experiment the severity factor (log R_0) was calculated according to Eq. (1). The last column in Table 1 presents the results for the normalized production on methane (FN) defined as the ratio between the production of methane for the treated and untreated wheat straw: (mL CH_4)$_{THi}$/(mL CH_4)$_{untreated}$.

Compared to the theoretical methane productivity (444 mL CH_4/g $VS_{removed}$), the experimental value obtained in the BMP test of the untreated wheat straw indicates that only 51% of the volatile solids were converted into methane. For the best thermal hydrolysis conditions (TH-7) the anaerobic biodegradability increased until a value of 61%.

Fig. 2 shows the relation between the severity factor and the normalized production of methane. The influence of the severity factor is quite clear: when increasing the severity factor, the production of methane increases until reaching a maximum. Over this optimum, the efficiency of the pretreatment decreases and therefore the methane production does, probably due to the formation of inhibitory compounds. For example, Thomsen et al. (2009) obtained an increase in the furfural concentration from 50 mg/L to 1200 mg/L when increasing the pretreatment temperature from 190 °C to 205 °C (6 min treatment).

In the present study, the highest improvement with respect to the untreated sample corresponds to the severity factor in the range 3.25–3.5.

Further analysis of the results is necessary in order to determine the best way of coupling temperature and time to get a desired severity factor (that is: short pre-treatment at high temperature,

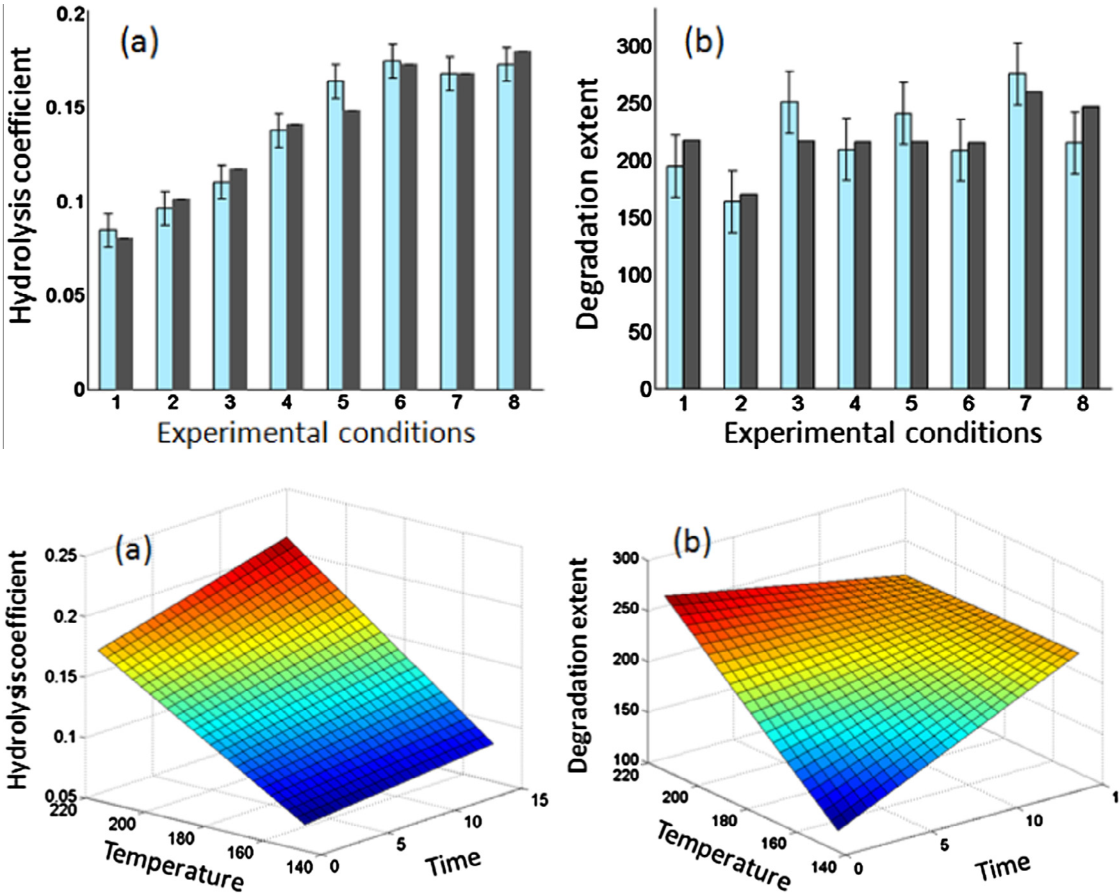

Fig. 4. Comparison between model prediction and the experimental data by using the optimal set of parameter values. (a) Hydrolytic coefficient (b) degradation extent. Light blue bars: real values, grey bars: predicted by the polynomial. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

or the contrary). Therefore, subsequent modeling and RSM evaluation was performed.

3.2. Modeling of the results and parameters determination

Fig. 3 presents the fitting process between the experimental methane production and the first order model curve. It can be observed that the model is able to reproduce the methane production profiles in a proper way since in most of the cases the model curve lies inside the corridor given by the standard deviation (SD). Moreover, the determination coefficients (R^2) are mostly above 0.98, which indicates that this model is able to explain around 98% of the experimental data variability. Table 2 shows the values obtained in the parameters estimation where it can be observed that the standard deviation of the estimated parameters was not significant with respect to the mean values, hardly over 10% compared to the optimized values, which is also an indicator of the model fitting procedure success.

With respect to the values of the parameters, the first order model fit shows that the thermal pretreatment had a positive influence on the hydrolysis rate (Fig. 3): this means that the higher the severity factor, the higher the hydrolysis constant. These results show that the solubilisation of particulate organic matter is a consequence of both temperature and time effects. Although the solubilized biomass is expected to be more available for the anaerobic biomass, the results show that in some cases the pretreatment lead to a decrease in biodegradability, especially for the highest severity factors. This can be explained due to the appearance of some recalcitrant compounds after the pretreatment, as aforementioned.

3.3. Response surface methodology (RSM) results

The parameters of the first order model were fitted to a polynomial equation to evaluate the influence of the two independent variables (temperature and time). The obtained equations are shown next:

$$K_H = 0.152 - 0.003 \cdot T + 0.0014 \cdot t + 0.000027 \cdot T \cdot t \tag{6}$$

$$B_0 = -249.48 + 31.58 \cdot T + 2.33 \cdot t - 0.1582 \cdot T \cdot t \tag{7}$$

In the operation range evaluated, the influence of the interactions between both parameters is low compared to the independent influence of each one. In the case of k_H, the determination coefficient (R^2) was 0.958, which means that the model correlates around 96% of the variability in the parameter. Therefore, this empirical model can be used to predict the hydrolysis constant using the data of temperature and pretreatment time within the studied design range. For B_0, the determination coefficient was not as good as expected (0.569), which may indicate that this type of polynomial model may not be the best option to predict this parameter. The results of the agreement between the k_H and B_0 values obtained from the BMP test and the predicted ones with the polynomial are presented in Fig. 4. Globally, there is a good agreement between the predicted and the actual values of the parameter, especially in the case of the hydrolysis constant.

By applying these polynomial equations, two surface responses were built in order to observe optimum region of the parameters in terms of temperature and time (Fig. 4). In the case of k_H, the optimum zone (red zone) can be observed toward the higher values of both temperature and time, which must entail that the soluble fraction of the organic matter increases when increasing these variables. By contrast for B_0, the best values were obtained at higher temperatures and short times. Therefore, the conclusion about the best way of coupling temperature and time to get the optimum severity factor around 3.5 is: high temperature (220 °C) and short time (1 min), instead of the contrary (lower temperature but higher time).

4. Conclusions

The influence of thermal pretreatment parameters (temperature and time) on the anaerobic biodegradation of wheat straw was evaluated. In terms of "severity factor", the optimum was obtained at 3.5, corresponding to 220 °C and 1 min treatment. A first order model fitted accurately the experimental results on biodegradability, confirming that the hydrolysis is the limiting step. A surface response methodology was applied to assess the combined effect of the temperature and the time on the kinetic parameters, which indicated that influence of the interactions between these variables is low in comparison with the separated influence of each one.

Acknowledgements

This work was financially supported by the company Cambi®, project "Thermal hydrolysis of solid wastes". The group of Valladolid University is Grupo de Excelencia GR 76 de la Junta de Castilla y León and member of the Consolider-Novedar framework (Programa Ingenio 2010). A. Donoso-Bravo is supported by the "Dirección de Investigación (DII)" of the Pontificia Universidad Católica de Valparaíso.

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Biomethane potential of wheat straw: influence of particle size, water impregnation and thermal hydrolysis

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PII: S1385-8947(13)01085-1
DOI: http://dx.doi.org/10.1016/j.cej.2013.08.041
Reference: CEJ 11145

To appear in: *Chemical Engineering Journal*

Received Date: 25 April 2013
Revised Date: 1 August 2013
Accepted Date: 12 August 2013

Please cite this article as: L.C. Ferreira, P.J. Nilsen, F. Fdz-Polanco, S.I. Pérez-Elvira, Biomethane potential of wheat straw: influence of particle size, water impregnation and thermal hydrolysis, *Chemical Engineering Journal* (2013), doi: http://dx.doi.org/10.1016/j.cej.2013.08.041

Biomethane potential of wheat straw: influence of particle size, water impregnation and thermal hydrolysis

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Abstract

The anaerobic digestion of organic wastes such as wheat straw represents a very interesting means of generating biogas while reducing the amount of waste to disposal. An enhancement in the hydrolysis limited digestion of straw can be achieved by optimizing operation and performing pre-treatments. In this study, the influence of particle size, water impregnation and thermal pre-treatment was investigated through biochemical methane potential tests (BMP). The maximum methane yield was obtained by heating the straw at 200ºC for 5 min followed by steam explosion, obtaining a 27% increase in methane productivity compared to non-treated straw (from 233 to 296 mL CH_4/gVS_{fed}). Cutting (3-5 cm) showed to be better than milling (<1 mm), and the impregnation of the straw with water helped to enhance BMP test results by 4-10% (supposed better mixing due to a 10 times reduction of solids concentration) but had no effect on thermal pre-treatment. On the contrary, the economic impact of milling and water addition on a thermal pre-treatment would be absolutely negative, increasing the operation cost necessary to reduce the size and to heat water, respectively.

Keywords: biochemical methane potential (BMP), particle size, thermal hydrolysis pre-treatment, wheat straw

1. Introduction

Wheat straw is the largest agricultural residue in Europe, and the second largest in the world, after rice straw [1, 2]. Nowadays straw is either used as bedding material for livestock, applied to the soil as natural fertilizer or as biomass for energetic valorization. The search for renewable energy sources together with the concern on greenhouse gas emissions have increased the interest on lignocellulosic materials as a source of energy [3, 4], which is particularly well suited for energy applications because of its large-scale availability, low cost and large production.

Anaerobic digestion of biomass is a more economical and environmentally beneficial way of biomass utilization compared to typical pathways to biodiesel or bioethanol [5]. However, the main obstacle impeding a more widespread application of straw as feedstock for anaerobic digestion is its low digestibility due to its refractory structure. Like other lignocellulosic biomass, wheat straw is a complex mixture of cellulose, hemicellulose and lignin. Bioconversion of wheat straw is favored because of its relatively low lignin content (15-20%) and high carbohydrate content (30-40 and 20-30 %w/w cellulose and hemicellulose, respectively) [6]. Lignin surrounds and seals the cellulose structure while hemicellulose serves as a connection between both of them [7]. Therefore, hydrolysis is a slow and difficult process [8, 9].

In order to improve the biodegradability of wheat straw, several methods have been investigated, such as mechanical size reduction from the organic particulate matter [10, 11, 12, 13], or the introduction of a lysis pre-treatment, such as physico-chemical alkaline dilution [14], microwave pre-treatment [15, 16] or thermal steam explosion [17, 18, 19]. This last option has proven to be very interesting, as it can be cost effective if a proper energy recovery is performed. Hydrothermal steam explosion is performed without the addition of chemicals or oxygen, representing a potential solution for the pre-treatment of large quantities of lignocellulosic biomass [1; 20].

In a steam explosion, biomass is heated and rapidly discharged to atmospheric pressure causing the explosion of the macromolecules, with the aim of upgrading the digestibility of lignocellulosic materials, by increasing porosity, removing lignin content and promote hemicellulose hydrolysis [18, 21]. Although the successful use of steam explosion has been proved from the point of view of fermentation and ethanol production [1, 22, 23, 24, 25], the evaluation of the methane potential of steam-exploded straw is more recent [19, 21, 26], and open to many other wastes (corn stover, maizecrop waste, rice straw, herbaceous waste, manure, sewage sludge).

The studies performed specifically with wheat straw [1, 18, 21] have shown that the effect of the thermal pre-treatment depends on several factors, such as chip size, temperature and time. It is generally accepted that there is an optimum temperature in the range of 150-220ºC and 5-20 minutes, but care must be paid for too severe treatments due to the formation of inhibiting phenolic and heterocyclic compounds, such as furfural [10].

Chip size is a crucial parameter, as any sort of cutting or milling is necessary to avoid clogging and heat transfer problems during thermal treatment (overcooking the outside of large chips and formation of inhibitory compounds). However, a promising finding is that enzymatic hydrolysis is improved for larger biomass particle sizes [27], as milling is an energy intensive and expensive process. Regarding the anaerobic digestion process, the effect of particle size reduction on methane yield of agricultural wastes is contradictory: positive in some studies [12, 28, 29], while negative in others [30, 31]. Therefore, the influence of particle size on wheat straw digestibility is still open to research.

The effect of water impregnation on thermal hydrolysis is a novel study in this paper. The impregnation of straw with acid or alkali has been successfully applied in enzymatic hydrolysis, while the influence of humidity on steam explosion effect is unexplored from the point of view of later methanization. From another point of view, dilution can be imperative to avoid overload or inhibition during the anaerobic digestion [32].

The aim of the present study is to evaluate the effect of particle size, dilution and thermal pre-treatment variables (temperature, time and water impregnation) on the biodegradability of wheat straw. For this purpose, batch anaerobic biodegradability tests were performed in order to check the biochemical methane potential (BMP) under different milling, washing and thermal hydrolysis conditions to determine individual and combined effects. Furthermore, a kinetic model has been used to obtain the specific rate constants to assess the relationship of the parameters evaluated.

2. Materials and Methods

2.1 Raw Material and experimental set-up

Wheat straw was grown in Valladolid (Spain), harvested in 2012 and characterized (Table 1). The original straw was ground (3-5 cm) or milled (<1 mm), according to the experimental set-up in Table 2.

Three series of experiments (A, B and C) were performed (Table 2) to cover the three scenarios to study: A. Influence of particle size and water dilution on wheat straw digestibility; B. Influence of steam explosion pre-treatment; and C. Influence of water impregnation time on thermal hydrolysis and digestion.

2.2 Particle size reduction and water impregnation

Based on bibliography (where references to particle sizes ranging from 0.2 mm to 10 cm can be found), two particle sizes were selected for series A: 3-5 cm pieces and powder < 1mm. In most of the references, the particle size influence is not assessed but established in the range of 1-5cm [12, 18, 21, 33].

The larger particle size was chopped with a cramp to get the desired interval 3-5 cm. A laboratory mill (Philips, HR7775) was used to grind the straw into a minor particle size (<1 mm) controlled with a sieve (CISA™). In the studies of series B and C only the major particle size were used.

Water addition in series A and C was performed by mixing the straw with water. In series A, the water was added when preparing the BMP tests (1:10 dilution), while in series C the straw was soaked for a desired washing time.

2.3 Thermal steam explosion pre-treatment unit plant

The pre-treatment was performed at the steam explosion pilot plant facility designed by Cambi AS and located at the wastewater treatment plant of Salamanca, Spain.

The steam explosion unit consists of a 30 L reactor vessel and a flash tank with a removable bucket to collect the pretreated material (Fig. 1). The steam is generated by a 25 kW electric steam boiler (200 L capacity) which can supply steam up to a maximum pressure of 34 bar (240ºC). Wheat straw is loaded into the reactor using a motorized ball valve (V1) at the top of the reactor. Steam is added to the reactor from the bottom, through an air-actuated valve (V2), heating the waste during the time established. The desired operation pressure (corresponding to a certain temperature) is set on the control panel unit, controlled automatically by the air-actuated valve (V2). For security reasons also a manual valve (V3) has to be opened to add steam to the pressure reactor. An air-actuated ball valve at the bottom of the vessel (V4) is responsible for the rapid pressure drop (explosion) and release of the pretreated biomass to the flash tank. The pretreated biomass is collected in a removable bucket at the bottom of the flash tank. Any steam that is not condensed leaves the unit via a carbon filter to remove smell.

In all the experiments, one kilogram of wheat straw was used. The reactor was fed to the unit and the reactor was pre-heated for 15 min before starting the experiments.

The effects of temperature and time were evaluated based on the severity factor (log R_0, Equation 1), which is the common term used in steam pre-treatments [11]

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \qquad \text{(Equation 1)}$$

where *t* is the time (min) and *T* the temperature (°C).

Different pre-treatment conditions were tested varying temperature (ranging 170-220ºC) and time (ranging 1-15 minutes), based on previous studies [14, 21, 26] concluding that the optimum severity factor (log R_0 – Equation 1) is in the range 3.3-3.6, and this criteria was considered to establish the combinations of temperature and time for series B.

2.4 Biochemical methane potential tests (BMP)

Batch anaerobic digestion tests were carried out in order to assess the wheat straw biodegradability after the different pre-treatment conditions applied. All tests were in triplicate in a 2 L borosilicate glass (260 mm height, 160 mm diameter and a 40 mm bottleneck) with 400 mL of a mixture of wheat straw and inoculum (with 12 g VS/kg and collected from a pilot digester treating waste activated sludge at 35ºC). The substrate to inoculum ratio (S/I) selected was 0.5 g VS/g VS as suggested in a previous researchers [32, 34]. A control test without substrate was included in order to check the methanogenic activity of the inoculum.

Before starting the test, the bottles were closed with ruber stoppers and aluminium crimps and degassed. Helium gas was circulated in the gas chamber for 5 minutes, and the test started after releasing the pressure. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1±0.3ºC), with constant mixing in a rotary desk. All the assays were finished when the methane production was below 5% of the total cumulative production.

The biogas volume was monitored by period measurements of the headspace pressure by a manually pressure transmitter (ifm, PN5007, range 1 bar).

The methane production of a control test performed with only inoculum was subtracted to obtain the real methane production from the straw. This value was finally expressed as specific methane yields (mL CH_4/g VS_{fed}), presented under standard temperature and pressure conditions (STP – 0ºC, 1 atm) defined by IUPAC (International Union of Pure and Applied Chemistry), and divided by the mass of volatile solids of substrate fed into to the assay.

The kinetics of methane production was calculated using a first-order model (Equation 2), applied successfully in other reports on anaerobic biodegradability tests [26, 35].

$$B = P.\left(1 - exp\left(\frac{-Rm\,(t-\lambda)}{P}\right)\right) \qquad \text{(Equation 2)}$$

Where *B* is the methane production (mL CH_4/gVS), *P* is the maximum methane production (mL CH_4/gVS), *Rm* is the maximum biogas production rate (mL CH_4/gVS·d), λ is the lag time (d) and *t* is the time of the assay (d). The data were analysed with Statgraphics® [36].

2.5 Analytical methods

Total and volatile solids (TS and VS) and total Kjeldahl nitrogen (TKN) were measured following the procedures given in Standard Methods for Examination of Water and Wastewater [37]. Total chemical oxygen demand (TCOD) was determined according to standard UNE 77004:2002 based in dichromate method [38]. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

3. Results and Discussion

3.1 Series A: Influence of particle size and dilution on wheat straw digestibility

Figure 2 and Table 3 present the results for the methane production curves (from BMP tests) and kinetic parameters for the series of tests A.

The results show that when adding water (tests A2-A4 compared to A1-A3) methane production slightly increased (4% increase for test A2 compared to A1, at 3-5cm straw size, and 10% increase for test A4 compared to A3, at 1mm straw size), and also did the production rate (5% increase for test A2 compared to A1, and 15% increase for test A4 compared to A3). The reason is probably related with a better mixing in the BMP tests performed with water (A2 and A4), as the solids concentration in the test decreased from 200g/kg to 20 g/kg.

Analyzing the influence of the particle size by comparing tests A1-A2 with A3-A4, it can be observed that the methane production was 5-13% higher for the larger particle size, and the kinetics were also faster. These results are in agreement with those obtained by De la Rubia et al. (2011) [30] for sunflower oil cake, and Izumi et al. (2010) [31] for food waste, but disagree with the results obtained by other authors.

Sharma et al. (1988) [39] found a significant increase in methane productivity of wheat straw by size reduction from 30 mm (192 mL/gVS) to 1mm (241 mL/gVS) but only a small effect for further size reduction to 0.1 mm. Hjorth et al. (2011) [29] obtained 70% increase in methane production for extruded straw respect non-extruded straw (150 mL/gVS), although no particle size values for treated straw are given. Friction heat and shear forces in the extruder could play an important role additional pre-treatment to the cutting. Palmowski and Müller (2000) [12] obtained 57% and 86% increase in methane yield for particles of 5 cm and 0.2 cm respectively, as compared to the untreated sample (182 mL/gVS).

Putting together these results with those obtained in the present research, it can be concluded that the composition of the biowaste should be assessed to compare small and large chip sizes, as the content of carbohydrates, proteins and lipids is not uniform in the different particle size fractions but have a clear different methane potential. If no organic matter is removed during the mechanical treatment cutting seems to be better to milling or grinding in order to minimize the energy input, as milling is not considered economically feasible due to the high energy requirements,

Based on these results, wheat straw with 3-5 cm was selected to be used in series B and C.

3.2 Series B: Influence of steam explosion pre-treatment

The results of the BMP tests performed for series B and the kinetic parameters obtained are presented in Figure 3 and Table 4, where B0 corresponds to non-treated wheat straw, cut to 3-5 mm.

In all steam-explosion experiments (B1-B3), the methane yield was higher than B0 (233 mL/dVS) in the range of 24-27% (288-296 mL/gVS). The kinetic study shows that the methane production rate was also 19-24% higher. Although similar results for tests B1-B2-B3, the highest productivity and production rate were for test B2, performed at 200ºC for 5 minutes (increase of 27% in the methane yield), corresponding to a severity factor (log R_0) of 3.64.

These results prove the effectiveness of the steam explosion pre-treatment, and concur with those obtained by other authors. The study published on methane production from steam-exploded wheat straw [21] agrees with the results obtained here. Bauer et al. (2009) [21] increased methane production from 275 to 331 mL/gVS when treating the straw at 180ºC for 15 minutes. [26] have previously optimized the pre-treatment conditions to a severity factor in the range 3.25-3.53, finding the optimum at 200ºC and 5minutes. This optimal agrees with the one here obtained.

3.3 Series C: Influence of water impregnation time on thermal hydrolysis

This series was conducted with 3-5 cm wheat straw thermally pretreated at 200ºC for 5 min (according to the optimum results for series A and B), with the objective of evaluating if water impregnation of wheat straw had any positive effect on the pre-treatment. The hypothesis that supports the theoretical possibility of increasing the steam explosion effect by washing the straw is the chance of the water to penetrate in the biomass structure, leading to a possible stronger lysis effect by steam explosion during the pressure drop.

Figure 4 and Table 5 present the results for the methane yield and kinetic parameters for series of tests C. The results show a negligible influence of the washing time on the thermal steam explosion pre-treatment, as the results obtained were very similar in the different tests. Only the kinetics showed to be slightly faster, but negligible. Therefore, the water added probably did not penetrate in the wheat straw structure, and did not help to disrupt the fibrils in the decompression step.

Although according to Jakoviak et al. (2011) [16], the humidity of the biomass may cause differences on the contents of cellulose and hemicellulose of wheat straw, the evaluation of the chemical composition of the straw in terms of lipids, carbohydrates and proteins would again be determining to confirm any hypothesis.

4. Conclusions

The methane production of 30-50 mm wheat straw pieces was 10.4% higher than the powder <1 mm. Therefore, for process performance and economics, cutting is desirable to milling. Thermal pre-treatment enhanced methane production by 19-24% for temperatures in the range 170-220ºC and 1-15 min heating time, being the optimum for 200ºC and 5 min, which increased methane yield by 27% (from 233 to 296 mL CH_4/gVS_{fed}). The impregnation of straw with water showed a poor positive effect in the BMP tests, but no effect on thermal steam explosion, apart from a clear worsening of the process economics if water was added.

Acknowledgments

This work was financially supported by the company Cambi (project "Thermal hydrolysis of solid wastes"). The research group is "Grupo de Excelencia GR76 de la Junta de Castilla y León" and member of the Consolider-Novedar framework.

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Figure captions

Figure 1 Cambi SA steam explosion unit. V - valves; VM - motorized valves; VA,B – one way valves; P – manometers to measure pressure; RD – safety valves; CF – carbon filter; TB-T – treated biomass tank; WT – Water tank

Figure 2 Methane yield for series A

Figure 3 Methane yield for series B

Figure 4 Methane yield for series C

Figures

Figure 1

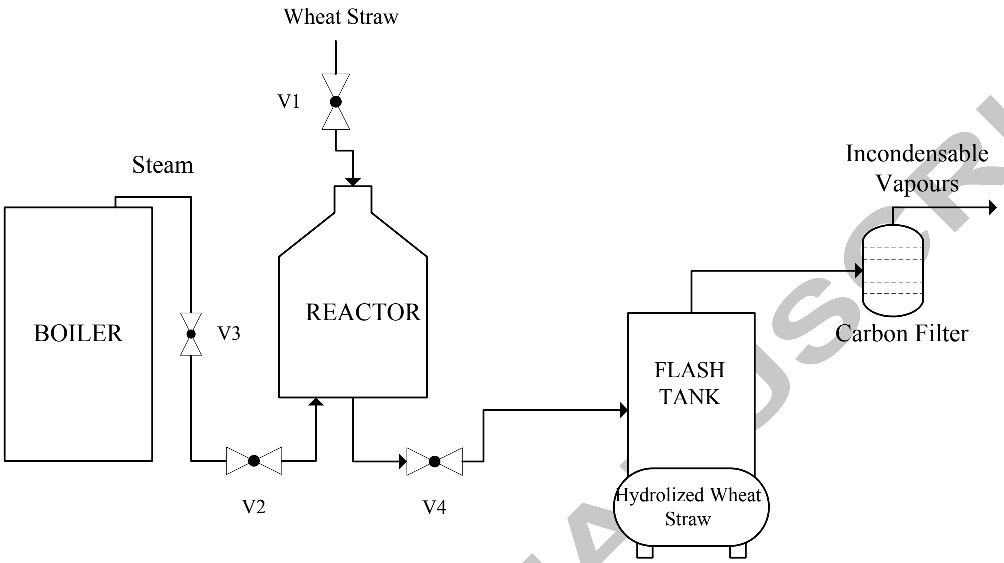


Figure 2

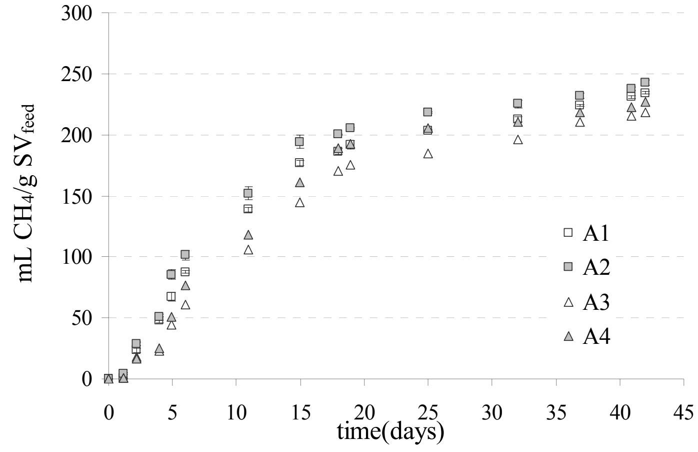


Figure 3

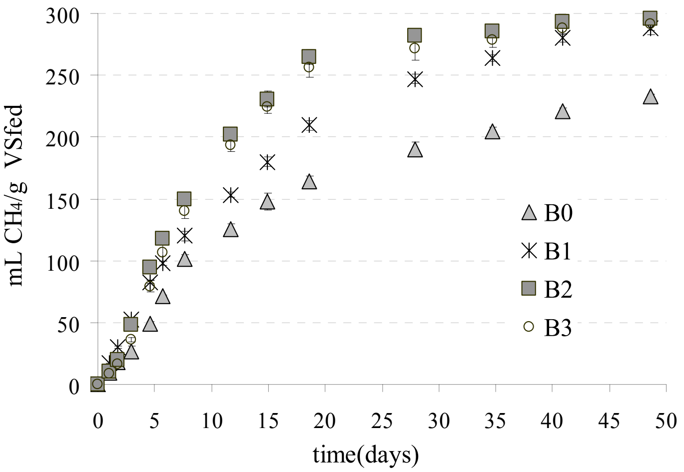
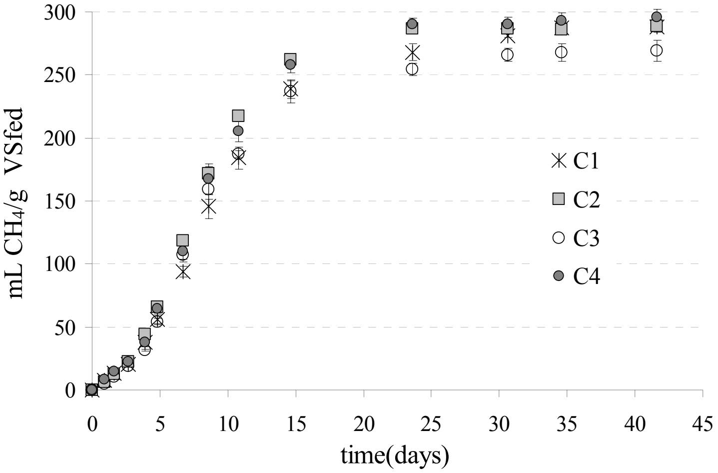


Figure 4


300
250
200
150
100
50
0
mL CH₄/g VSfed
0
5
10
15
20
25
30
35
40
45
time(days)
C1
C2
C3
C4

Tables

Table 1. Average characteristics of the original wheat straw

	TS (g/kg)	VS (g/kg)	TCOD (g/kg)	TKN (g N/kg)	TOC (% weigh)	C/N
Series A-B	895 ± 11	821 ± 9	1075 ± 8	4.723	43.2 ± 0.3	92
Series C	924 ± 9	846 ± 5	1089 ± 6	4.578	43.4 ± 0.2	92

Table 2. Experimental set-up

Series A			Series B				Series C			
Test	Particle size	Dilution	Test	T (ºC)	t (min)	log R_0	Test	T (ºC)	t (min)	Washing time (h)
A1	3-5 cm	No	B0	Untreated			C1	200	5	0
A2	3-5 cm	Yes	B1	170	15	3.2	C2			3
A3	<1mm	No	B2	200	5	3.6	C3			12
A4	<1mm	Yes	B3	220	1	3.5	C4			24

Table 3. Results for methane yield and kinetic parameters for series A

Parameter	A1	A2	A3	A4
P (mL CH_4/gVS) [a]	239	245	232	239
Rm (mL CH_4/gVS.d) [b]	20.2	23.2	15.9	18.3
λ (day) [c]	0.9	0.8	1.2	1.2
R^2	0.996	0.994	0.991	0.988

[a] P: maximum methane production; [b] Rm: maximum biogas production rate; [c] λ: lag time (according to Equation 2)

Table 4. Results for methane yield and kinetic parameters for series B

Parameter	B0	B1	B2	B3
P (mL CH_4/gVS) [a]	245	291	304	301
Rm (mL CH_4/gVS.d) [b]	16.1	20.6	28.5	26.2
λ (day) [c]	0.8	0.4	0.9	1
R^2	0.985	0.997	0.995	0.991

[a] P: maximum methane production; [b] Rm: maximum biogas production rate; [c] λ: lag time (according to Equation 2)

Table 5. Results for methane yield and kinetic parameters for series C

Parameter	C1	C2	C3	C4
P (mL CH_4/gVS) [a.]	316	315	293	323
Rm (mL CH_4/gVS.d) [b.]	23.4	28.2	24.4	26.7
λ (day) [c.]	1.3	1.3	1.4	1.3
R^2	0.971	0.963	0.962	0.964

[a.] P: maximum methane production; [b.] Rm: maximum biogas production rate; [c.] λ: lag time (according to Equation 2)

Highlights

- Assessment of the influence of thermal pretreatment on the anaerobic biodegradation of wheat straw
- Optimum severity factor at 200ºC and 5 minute (3.6 severity factor)
- Evaluation through BMP tests: 27% increase in methane productivity of steam exploded straw respect untreated straw
- Cutting (3-5 cm) wheat straw showed to be better than milling (< 1mm)

Elsevier Editorial System(tm) for Waste Management
Manuscript Draft

Manuscript Number:

Title: Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure

Article Type: Full Length Article

Keywords: biochemical methane potential, thermal hydrolysis, pretreatment, methane yield, pig slurry; steam-explosion

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Abstract: The assessment of the biodegradability of thermal steam-exploded pig manure was performed compared to untreated samples. The pre-treatment was performed under different combinations of temperature and time, ranging 150-180ºC and 5-60 minutes, and used as substrate in a series of batch biochemical methane potential (BMP) tests. Results were analyzed in terms of methane yield, kinetic parameters and severity factor. In all the pre-treatment conditions, methane yield and degradation rates increased when compared to untreated pig slurry. An ANOVA study determined that temperature was the main factor, and the optimum combination of temperature - time of pretreatment was 170 ºC - 30 minutes, doubling methane production from 159 to 329 mL CH4/gVSfed. These operation conditions correspond to a severity factor of 3.54, which was considered an upper limit for the pretreatment due to the possible formation of inhibitory compounds, hindering the process if this limit is trespassed.

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Cover Letter

Department of Chemical Engineering and Environmental Technology
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Dear Editor,

Please, find attached the manuscript "**Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure**", co-authored by Liliana Catarina Ferreira, Theo Syrto Octavio de Souza, Fernando Fernández-Polanco and Sara Isabel Pérez-Elvira. This original manuscript is submitted for publication in **Waste Management**, where it has not been previously submitted.

In this research, the thermal hydrolysis of the separated solid fraction of pig manure prior to anaerobic digestion was evaluated through the operation of a thermal hydrolysis pilot plant. Although the thermal hydrolysis technology has been successfully operated for treating sludge (even developed full-scale), the application to other wastes is unexplored, and is of great interest for companies exploiting this technology.

Therefore, this is an innovative study, of great potential interest, combining two crucial aspects to improve the poor anaerobic biodegradability of this type of waste: the digestion of the separated slurry and the introduction of a pretreatment. The result presented in the paper is a double methane potential of the waste.

The main novelties of the paper compared to other references on the topic are:

- Combination of thermal hydrolysis and steam-explosion, as full scale devices. All the works published up to now only cook the manure in an autoclave or similar, but do not use steam and steam-explosion).
- Optimization of both temperature and time. While most of the papers just consider the effect of temperature

For these reasons, this paper is as a reference for scientific audience, as the pre-treatment of organic wastes is a growing field (after a huge research on sewage sludge pretreatments), but has also a great interest as a basis to perform an energetic-economic evaluation on the application of the technology to manure, opening the possibility of the current technology.

I am available as a reviewer for WM during the current and the following years.

We look forward to your evaluation.

Kindest regards,

Sara Isabel Pérez Elvira

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Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure

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Abstract

The assessment of the biodegradability of thermal steam-exploded pig manure was performed compared to untreated samples. The pre-treatment was performed under different combinations of temperature and time, ranging 150-180ºC and 5-60 minutes, and used as substrate in a series of batch biochemical methane potential (BMP) tests. Results were analyzed in terms of methane yield, kinetic parameters and severity factor. In all the pre-treatment conditions, methane yield and degradation rates increased when compared to untreated pig slurry. An ANOVA study determined that temperature was the main factor, and the optimum combination of temperature - time of pretreatment was 170 ºC - 30 minutes, doubling methane production from 159 to 329 mL CH_4/gVS_{fed}. These operation conditions correspond to a severity factor of 3.54, which was considered an upper limit for the pretreatment due to the possible formation of inhibitory compounds, hindering the process if this limit is trespassed.

Keywords: biochemical methane potential, thermal hydrolysis, pretreatment, methane yield, pig slurry; steam-explosion

1. Introduction

In Spain, currently the second largest producer of pig manure in the European Union (PNIR, 2007-2015), manure management has become an environmental issue. The traditional application of manure is as land fertilizer (Schöder, 2005), contributing to maintaining the soil organic carbon and nutrients stocks. However, due to the intensification of livestocks production, in many areas the organic waste nutrients exceed the requirement for crop production (Wnetrzak et al., 2013), resulting in groundwater contamination, nitrates leaching and eutrophication. Therefore, any kind of treatment for pig wastes must be implemented according to the environmental legislation, such as the EU Nitrates Directive (S.I. NO. 610, 2010).

The valorization of the organic matter content in pig manure to biogas through anaerobic digestion (AD) is a very interesting option (Krishania et al., 2013; Mata-Alvarez et al., 2000), although ammonia inhibition issues have to be taken into account for considering manure as a sole substrate (Hansen et al., 1998). However, similar to other types of organic wastes, biogas production from pig manure is relatively low: from 290 to 550 L CH_4/kg of organic matter (Burton and Turner, 2003), due to the limiting hydrolysis step of the fiber content (Menardo et al., 2012). Some treatment options are reported to increase AD performance, such as acidification (Moset et al., 2012; Sutaryo et al., 2013) or separation of solid and liquid fractions (Fangueiro et al., 2012; Møller et al., 2007).

Thermal pre-treatment appears as a very interesting option and a potential solution for a large quantity of lignocellulosic biomass. The use of a thermal pre-treatment to enhance the anaerobic digestion of sewage sludge is reported in several references (Pérez-Elvira et al., 2011; Bougrier et al., 2008), and has been developed full scale. However, the application to other organic wastes such as agricultural wastes (Ferreira et al., 2013; Qiao et al., 2011) or manure is very recent, and still open to research. Some references can be found concerning thermal pretreatment to chicken manure (Ardic and Tarner, 2005; Bujoczek et al., 2000), swine manure (Mladenovska et al., 2006; Chae et al., 2008), dairy manure (Yoneyama et al., 2006; Rico et al., 2011; Rico et al., 2012) and pig manure (Bonmati et al., 2001; Cuetos et al., 2008; Carrère et al., 2009; Menardo et al., 2011). In the references found on thermal pre-treatment of manure the study was performed considering only the effect of temperature (with or without chemicals), but no evaluation on the influence or optimization of temperature-time combinations are reported.

Finally, the application of any thermal technology requires to concentrate the waste (Pérez-Elvira & Fdz-Polanco, 2012). Several references can be found about separation of solid and liquid fractions of pig slurry in order to economize transport or increase the energy potential through biogas production (Møller et al., 2007; Nolan et al., 2012; Xie et al., 2012).

The aim of this study was to evaluate the methane yield of steam exploded pig slurry (separated solid fraction of pig manure) under different temperature-time combinations, compared to a control of untreated slurry. BMP tests were performed and kinetic parameters were evaluated.

2. Material and Methods

2.1 *Manure samples: thickening and characterization*

Pig slurry was collected from a piggery in Segovia (Spain) and characterized before ("original sample") and after centrifugation at 5000 rpm for 5 min ("solid fraction"). Table 1 presents the results from the analytical characterization.

As expected, the concentrated pig slurry (manure) presented a higher percentage of volatile solids, which means a higher content of organic matter. The C/N ratio increased when compared to the original sample, which allows better conditions for the treatment.

2.2 *Thermal pretreatment pilot plant and operation conditions*

As shown in Figure 1, the thermal hydrolysis plant consisted of a reactor (2L) connected to a boiler by a control valve (V1) and to a flash tank (5L) by a decompression valve (V2). The operation was batch: 250g of pig manure were fed to the reactor, and then heated with steam from the boiler (180ºC, 10 bar) for the desired period of time. Once completed the operation time, the steam inlet (V1) is closed and the decompression valve (V2) is opened in a sudden decompression, releasing the hydrolysed pig slurry to the atmospheric flash tank. Before starting the experiments, the reactor was pre-heated for approximately 5 min at the same temperature selected for the pretreatment, in order to minimize condensation.

Different pretreatment conditions were tested varying both temperature (ranging from 120-180ºC) and time (ranging from 5-60 minutes), in a total of 15 different operation conditions (Table 2). The combination temperature and time of pretreatment define the severity factor (log R_0, eq. 1). This parameter is most widely accepted for steam pretreatments (Hendriks and Zeeman, 2009) to express the severity of the pretreatment.

$$\log R_0 = \log\left(t.exp\left(\frac{T-100}{14.75}\right)\right) \qquad (1)$$

in which *t* is the time (min) and *T* the temperature (°C), 100 is the base temperature (100ºC), and 14.75 is the activation energy based on the assumption that the reaction is hydrolytic and the overall conversion is first order (Xu et al., 2011). This expression only takes into account time and temperature, and does not consider the effect of the flash. The study of this effect was not assessed in this paper.

Theoretically, the more severe the pretreatment, the more organic matter is made available for digestion. However, very severe pretreatments can lead to formation of inhibitory compounds from the macromolecules, driving to an indirect relationship between the severity factor and the biodegradability. Therefore, there should be an optimum value for the severity factor.

2.3 *Anaerobic biodegradability*

Biochemical methane potential (BMP) tests were carried out in triplicate to assess the pig slurry biodegradability before and after the different pretreatment conditions applied, following standardized methodology (Angelidaki et al., 2009). A control test without substrate was included in order to check the methanogenic activity of the inoculum. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1±0.3ºC), with constant mixing in a shacker desk.

The anaerobic inoculum used was taken from a pilot sludge digester treating activated sludge (containing 12 $gVS.kg^{-1}$) and pre-incubated for four days (35.1±0.3ºC) in order to minimize its residual biodegradable organic matter content.

Borosilicate glasses of 300mL volume were used in the BMP tests, with a reaction volume of 110mL in order to have enough headspace for biogas accumulation. The substrate/inoculum (S/I) ratio selected was 0.5 $gVS.(gVS)^{-1}$, as suggested by Neves et al. (2004) and Angelidaki et al. (2009).

Biogas production was measured manually by a pressure transmitter (ifm, PN5007, range 1 bar) in the headspace of each reactor. From the biogas production curves, the specific methane yield (mL CH_4/gVS_{fed}) was calculated at test-day 20 under standard temperature and pressure conditions (STP – 0ºC, 1 atm) defined by IUPAC (International Union of Pure Applied Chemistry), by dividing the methane production due to the substrate (once subtracted the production due to the inoculum) by the quantity of volatile solids of substrate fed to the test ($mL_{substrate}$ x g VS/$mL_{substrate}$).

2.4 *Analytical Methods*

Substrates, inoculum and digestates were characterized in all the experiments. Total and volatile solids (TS and VS, respectively) and total kjeldahl nitrogen (TKN) were measured following the procedures given in the *Standard Methods for Examination of Water and Wastewater* (APHA et al., 2005). Chemical oxygen demand (COD) was determined according to standard UNE 77004:2002 based in the dichromate method. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

2.5 *Data analysis and kinetic approach*

Apart from obtaining the specific methane yields (mL CH_4/gVS_{fed}), a kinetic approach was also employed to analyze the obtained data. The kinetics of methane production were calculated using a reaction curve-type model (eq. 2), applied successfully in other studies regarding anaerobic biodegradability tests (Ferreira et al., 2013).

$$B = P.\left(1 - exp\left(\frac{-Rm(t-\lambda)}{P}\right)\right) \quad (2)$$

in which *B* is the methane production (mL CH_4/gVS), *P* is the maximum methane production (mL CH_4/gVS), R_m is the maximum methane production rate (mL CH_4/gVS·d), λ is the lag time (d) and *t* is the time of the assay (d). The data were analyzed with Statgraphics®.

Finally, to evaluate the influence of temperature and time of pretreatment on methane production, the results obtained were compared by the analysis of variance methodology (ANOVA), using Microsoft Excel®, with a confidence level of 95%.

3. Results and Discussion

3.1 *Batch tests and methane yield*

Figure 2 presents the evolution of methane productivity (mL CH_4/gVS_{fed}) in all the BMP assays performed, compared to the control untreated substrate (TH0). For better comparison, Table 2 present the final specific methane yield improvements respect the control as normalized production of methane (FN), defined as the ratio at day 20 between the production of methane for the treated and untreated waste, $(mL\ CH_4)_{THi}/(mL\ CH_4)_{untreated}$.

3.2 *Evaluation of temperature-time combinations*

An initial evaluation of the results presented in the “Experimental results” column of Table 2 show that all the pre-treatments performed (TH1-TH15) enhanced the initial biodegradability of the pig slurry (TH0), from 26% (120ºC, 5 min) to 107% (170ºC, 30 min), being the latter the best pre-treatment condition evaluated. Comparing the influence of temperature and time, it can be observed a different behaviour depending on the temperature level. For low temperatures (120ºC), the influence of pre-treatment time was the most noticeable. For moderate temperatures (150ºC), the influence of the pre-treatment time was not so strong. For high temperatures (170 and 180°C), time played a crucial role from the point of view of inhibition. Pre-treatment times over 30 minutes at 170ºC or over 15 minutes at 180ºC caused a reduction in methane yield, probably due to the formation of inhibitory compounds.

Based on this qualitative analysis, a quantitative analysis of variance was performed. The data concerning pre-treatment time of 60 min were not considered for this study, as methane yield was mostly inhibited. The results of the ANOVA study showed that in all cases temperature caused significant statistical difference between data (F_{ratio} = 6.29, $F_{critical}$ = 4.76), while pre-treatment time did not (F_{ratio} = 2.81, $F_{critical}$ = 5.14). This indicates that, when dealing with both variables, temperatures should be considered as the main parameter as the basis to define the best pre-treatment time.

Figure 3 presents a graphical approach of the effect of both temperature and time on FN. It can be observed that the best improvements in methane yield are centered in the combination 170°C, 30 min, which is in accordance to the globally accepted values regarding thermal hydrolysis of sludge (Fdz-Polanco et al., 2008). This suggests that these thermal hydrolysis conditions are the optimum for enhancing the methane yield of concentrated pig slurry.

3.3 Evaluation of kinetic parameters

The kinetic parameters obtained by fitting equation 2 to the experimental data on methane production are presented in the "Kinetic parameters" column of Table 2. The results obtained concerning the maximum methane production (P) match with those previously discussed: increase for temperature and time increase, but decreasing trend for the longest times at temperatures above 170ºC. However, maximum methane production rates (R_m), seemed to differ slightly from this trend. The highest value of R_m was obtained for 150°C, 60 min, and lower R_m values were obtained for higher temperatures. And, again, pre-treatment times over 30 minutes for 170ºC and over 15 minutes for 180ºC caused a reduction in methane production rates.

Figure 4 present the effect of temperature and time on R_m. Although similar to Figure 2 with respect to the optimum (170ºC, 30 minutes), the trend for higher temperature-time values is different. These results suggest that inhibition of the maximum methane production is not necessarily coupled to lower degradation rates in the same levels. Even with the formation of refractory compounds due to high temperatures and pretreatment times, those conditions might still be able to improve rates, leading to reduced size of digesters as one possible advantage. However, a precise choice would depend on economic studies that take into account several variables and the process as a whole.

3.4 Evaluation of the severity factor

Figure 5 presents the relationship between the severity factor and the normalized production of methane (FN). The influence of the severity factor on the response of the methane yield presents some differences when temperature and time change. For temperatures of 120 and 150°C, it is clear by Figure 5 that FN always increases with the severity factor. However, for the higher temperatures of 170 and 180°C, there is a limit in the severity factor that, once surpassed, a reduction in FN occurred. According to Figure 5 and Table 2, the optimum value for the severity factor would be 3.54 for a temperature of 170°C. For a temperature of 180°C, however, this severity factor led to lower values of FN.

For higher values of the severity factor, inhibition in methane production was observed. This suggests that a severity factor of 3.54 could be considered an upper limit in which some instability in performance may be expected depending on operational conditions.

Conclusions

The influence of thermal pretreatment parameters (temperature and time) on the anaerobic biodegradation of the solid fraction of pig slurry was evaluated. All the conditions tested were better than the untreated condition, which means that the thermal pretreatment improved the anaerobic digestion of this type of waste, not only concerning biodegradability, but also degradation rates. Results suggested that temperature has a greater effect on methane yield than pretreatment time, and that the best combination of parameters would be 170^{o}C and 30 min, which was able to maximize methane production up to 200% when compared to untreated samples (from 159 to 329 mL CH_4/gVS$_{fed}$). This corresponds to a severity factor of 3.54, which seemed to be an upper limit not to be trespassed to avoid the formation of inhibitory compounds.

Acknowledgments

This work was financially supported by the company Cambi®, project “Thermal hydrolysis of solid wastes”. The group of Valladolid University is *Grupo de Excelencia GR 76 de la Junta de Castilla y León* and member of the Consolider- Novedar framework (Programa Ingenio 2010).

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Figure captions

Figure 1 – Thermal steam-explosion pilot plant

Figure 2 – BMP assays for the different experimental conditions applied

Figure 3 – Effect of temperature and time of pretreatment on FN. Darker areas mean regions in which values of FN are higher

Figure 4 – Effect of pre-treatment temperature - time combinations on the methane production rates (R_m). Darker areas mean regions in which values of R_m are higher

Figure 5 - Normalized methane productivity (FN [$(\text{mL CH}_4)_{\text{THi}}/(\text{mL CH}_4)_{\text{untreated}}$]) with respect to the severity factor (log R_0)

Highlights

- Assessment of the influence of a thermal steam-explosion pretreatment on the anaerobic biodegradation of the separated solid fraction of pig manure
- Novel study in evaluating the influence of both temperature (ranging 150ºC-180ºC) and time (ranging 5-60 minutes)
- The thermal pretreatment improved the anaerobic digestion of this type of waste, not only concerning biodegradability, but also degradation rates.
- Optimum at 170ºC and 30 minutes (3.54 severity factor): double methane productivity compared to untreated manure (increase from 159 to 329 mL CH_4/gVS_{fed})

Figures

Figure 1

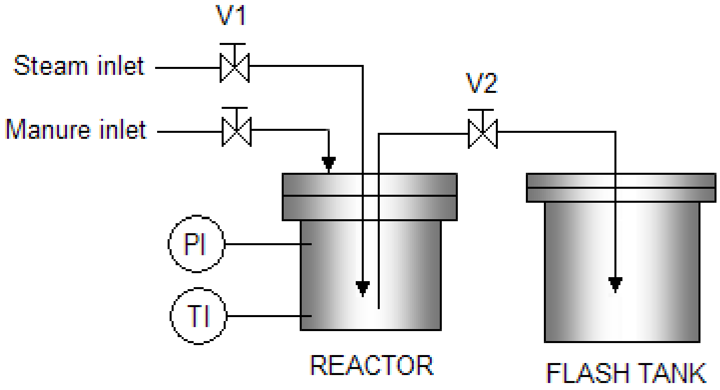


Figure 2

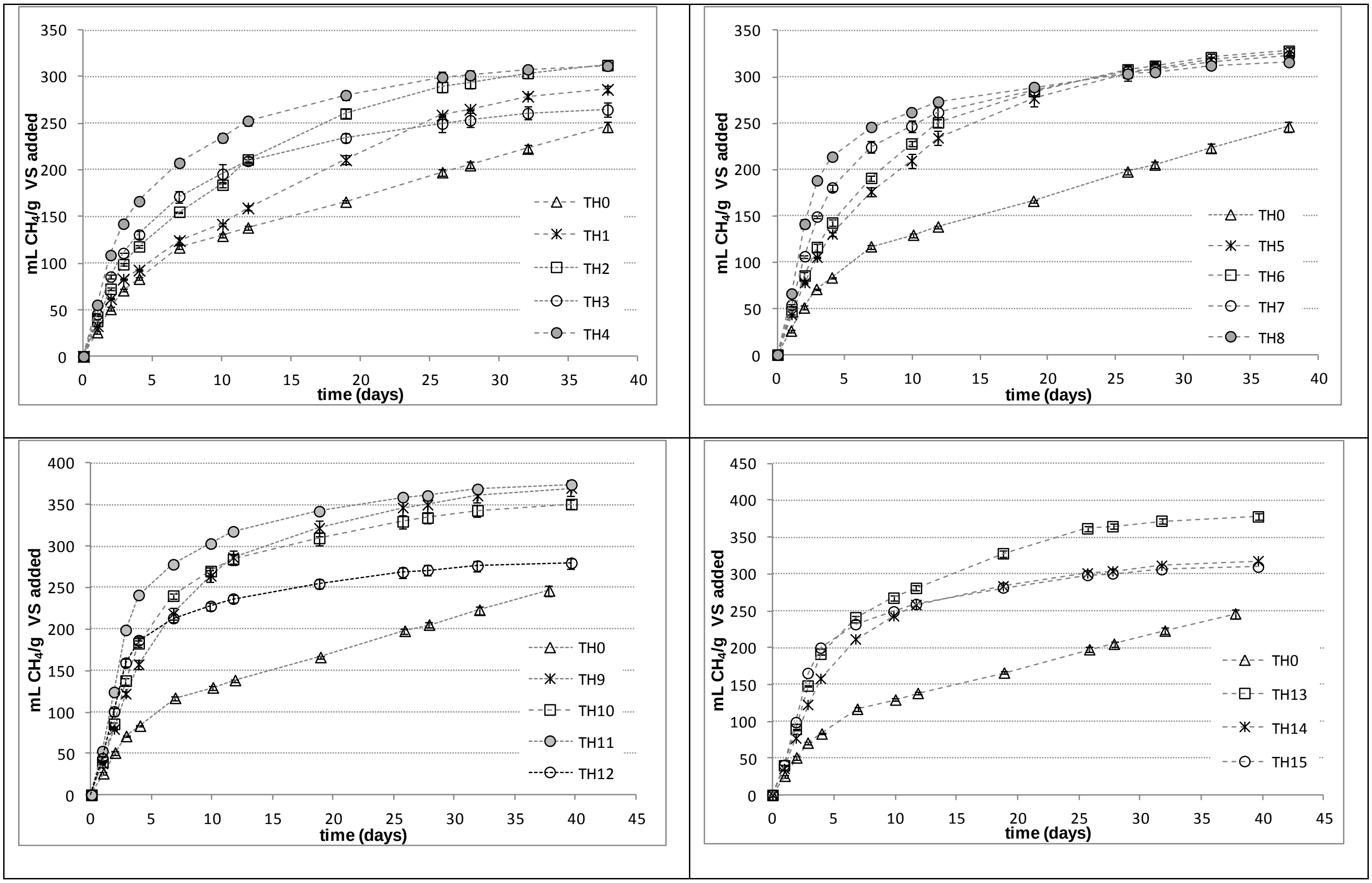

mL CH$_4$/g VS added
time (days)
0
50
100
150
200
250
300
350
400
450
0
5
10
15
20
25
30
35
40
45
TH0
TH1
TH2
TH3
TH4
TH5
TH6
TH7
TH8
TH9
TH10
TH11
TH12
TH13
TH14
TH15

Figure 3

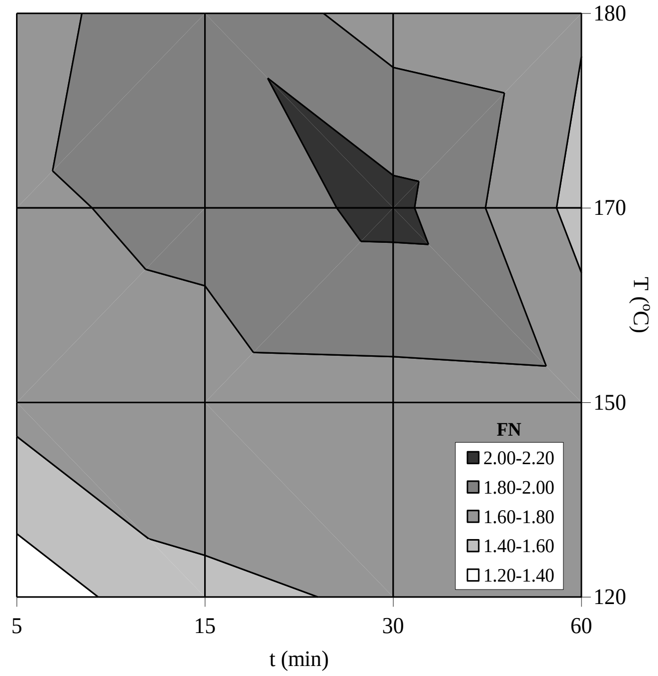

180
170
150
120
T (°C)
5
15
30
60
t (min)
FN
2.00-2.20
1.80-2.00
1.60-1.80
1.40-1.60
1.20-1.40

Figure 4

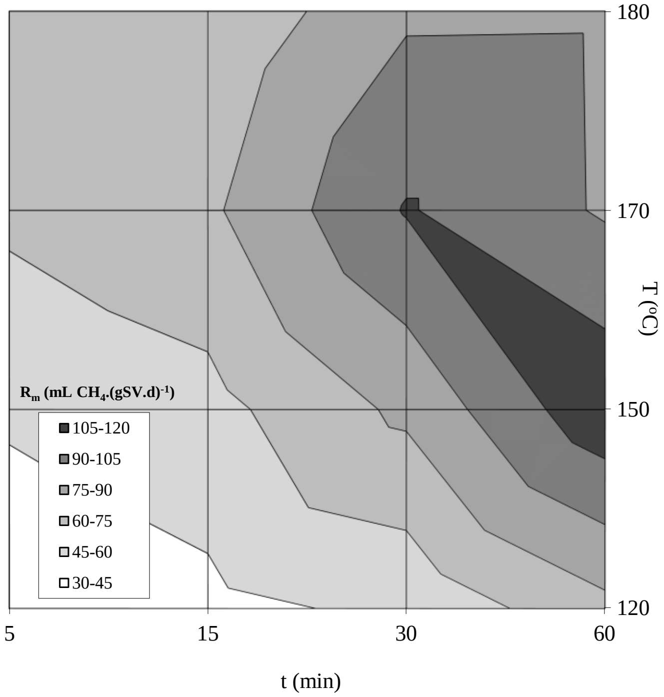
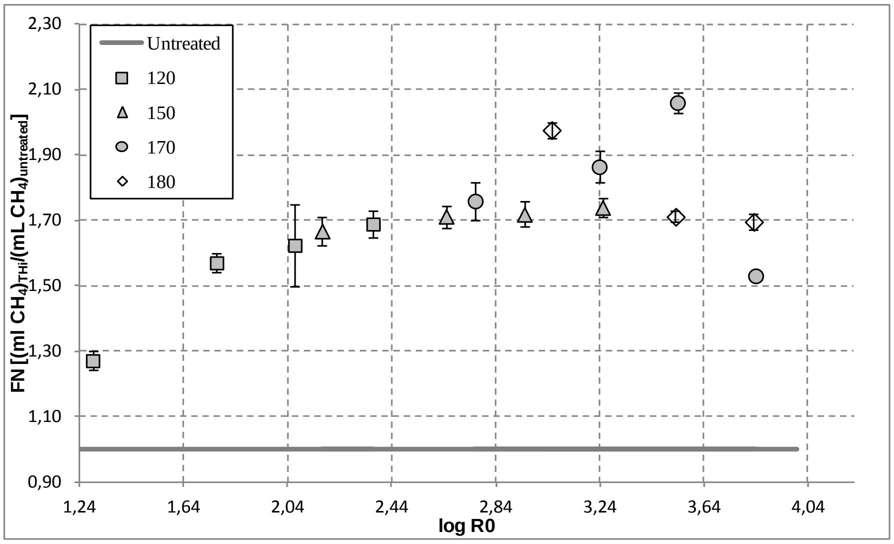

180
170
150
120
T (°C)
5
15
30
60
t (min)
R_m (mL CH4.(gSV.d)-1)
105-120
90-105
75-90
60-75
45-60
30-45

Figure 5



Untreated
120
150
170
180
FN [(ml CH$_4$)$_{THi}$/(mL CH$_4$)$_{untreated}$]
2,30
2,10
1,90
1,70
1,50
1,30
1,10
0,90
1,24
1,64
2,04
2,44
2,84
3,24
3,64
4,04
log R0

Tables

Parameter		Original sample	Solid fraction	Units
Total solids	TS	46.6 ± 2.1	166.4 ± 0.2	g/kg
Volatile Solids	VS	36.8 ± 2.7	138.6 ± 0.2	g/kg
Percentage of VS	% VS	79	83	-----
Chemical oxygen demand	COD	54.20 ± 0.8	197 ±3	gO_2/kg
Total kjeldahl nitrogen	TKN	7.40	6.05	gN/kg
Total organic carbon	TOC	6.29	7.48	% weight
Ratio C/N	C/N	8.5	12.4	-----
Ammonium	NH_4^+	4671	-----	gNH_4^+-N/g
Ratio COD/VS	COD/VS	1.47	1.42	-----

Table 1 Average characteristics of the original sample and solid fraction of pig manure (before and after centrifugation, respectively).

Experimental Results					**Kinetic Parameters**			
TH i	**T (ºC)**	**t (min)**	**Severity Factor ($\log R_0$)**	**FN**	**Rm mL CH_4/gVS$_{fed}$.d**	**λ (d)**	**P mL CH_4/gVS$_{fed}$**	**R square**
TH0	0	0	0.00	1.00	32.1	0.22	159	0.9852
TH1	120	5	1.29	1.26	31.6	0.10	200	0.9547
TH2	120	15	1.76	1.59	41.2	0.15	253	0.9737
TH3	120	30	2.07	1.63	48.2	0.12	259	0.9684
TH4	120	60	2.37	1.67	70.8	0.22	265	0.9821
TH5	150	5	2.17	1.70	47.9	0.21	271	0.9825
TH6	150	15	2.65	1.75	55.0	0.25	278	0.9876
TH7	150	30	2.95	1.72	78.3	0.32	273	0.9893
TH8	150	60	3.25	1.72	116.3	0.38	274	0.9875
TH9	170	5	2.76	1.84	63.1	0.45	292	0.9973
TH10	170	15	3.24	1.93	72.3	0.47	308	0.9950
TH11	170	30	3.54	2.07	106.1	0.45	329	0.9868
TH12	170	60	3.84	1.53	88.3	0.45	244	0.9844
TH13	180	5	3.05	1.99	70.6	0.39	317	0.9863
TH14	180	15	3.53	1.77	62.4	0.45	282	0.9971
TH15	180	30	3.83	1.70	87.7	0.47	271	0.9839

Table 2 Thermal conditions applied, experimental results and kinetic parameters for the different experiments performed

Bioresource Technology 148 (2013) 317–324

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Thermal pretreatment and hydraulic retention time in continuous digesters fed with sewage sludge: Assessment using the ADM1

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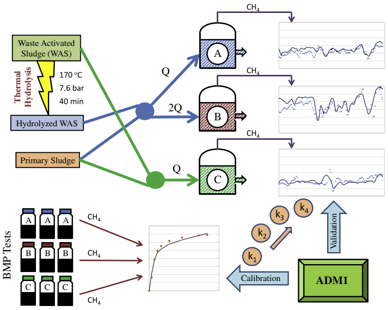
HIGHLIGHTS

- The behavior of three pilot-scale sludge digesters was evaluated through modeling.
- The ADM1 was able to predict the effects of thermal pretreatment and HRT changes.
- Increases in the disintegration coefficient due to pretreatment were observed.
- Model under/overestimation lower than 15% regarding CH_4 production.
- The ADM1 showed to be accurate and useful to predict the studied conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 July 2013
Received in revised form 29 August 2013
Accepted 31 August 2013
Available online 7 September 2013

Keywords:
ADM1
Anaerobic digestion
Modeling
Sludge pretreatment
Thermal hydrolysis

ABSTRACT

Thermal pretreatment is an interesting technique not only for increasing sludge biodegradability, leading to higher methane productivity, but also for improving degradation rates, allowing full-scale plants to reduce the size of digesters. In this study, the Anaerobic Digestion Model No. 1 (ADM1) was used as a tool to assess the effects of thermal pretreatment and hydraulic retention time (HRT) on the performance of three pilot-scale digesters fed with mixed sludge with/without pretreatment applied to the waste activated sludge fraction. Calibration procedures using batch tests showed an increase of up to five times in the model disintegration coefficient due to the pretreatment, and the validations performed presented good accuracy with the experimental data, with under/overestimation lower than 15% in both average and global accumulated CH_4 productions. Therefore, the ADM1 demonstrated its feasibility and usefulness in predicting and assessing the behavior of the digesters under these conditions.

1. Introduction

Wastewater treatment plants (WWTPs) based on the activated sludge system as the core unit are globally spread, due to its reliability and efficiency in a wide range of environmental and operational conditions. However, this alternative presents two main economical drawbacks: aeration costs and large volume of sludge to be disposed. The disposal of primary and waste activated sludge (PS and WAS, respectively) may represent up to 50% of the total operating costs of WWTPs (Appels et al., 2008), and thus attention must be strongly directed in this regard. Among the procedures for sludge stabilization, anaerobic digestion (AD) is commonly applied, with advantages including lower costs and conversion of organic matter to methane, which can be used for energy generation. Sludge biodegradability and degradation rates are a matter of concern, though, and inherently linked to AD energy integration and economic viability. WAS is mainly composed of microbial cells/flocs, presenting low biodegradability, especially when produced by activated sludge systems operated with extended aeration; in contrast, PS is more biodegradable (Carlsson et al., 2012). Nevertheless, both may be mixed and

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0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.08.161

thickened for further treatment (Carrère et al., 2010). Increasing the degradation extent and rates, leading to improved methane production, solids reduction and overall process optimization, is therefore of paramount importance in sludge management.

Several sludge pretreatment techniques have been studied in the past years, with the purpose of improving AD of sludge and other substrates. They include thermal, mechanical, chemical, biological, wet oxidation, freeze/thaw, microwave and pulsed electric field pretreatments (Carrère et al., 2010; Bordeleau and Droste, 2011; Carlsson et al., 2012). Among the available alternatives, thermal hydrolysis has been shown to be of particular interest to improve the AD of WAS (Li and Noike, 1992; Fdz-Polanco et al., 2008). Thermal hydrolysis may account for an improvement of up to 100% in biogas production (Li and Noike, 1992; Carrère et al., 2010), with additional solids reduction, pathogens elimination (Pérez-Elvira et al., 2011) and increase in dewaterability (Neyens and Baeyens, 2003). Increase in biodegradability and degradation rates, and subsequent improvements in methane production, are related mainly to COD solubilization when thermal pretreatment is applied (Carlsson et al., 2012). Temperatures usually between 160 and 180 °C, pressures of 600–2500 kPa and treatment times of 30–60 min (Carrère et al., 2010) are able to disrupt cell walls and flocs, solubilizing organic matter and increasing the hydrolytic limiting-step considered responsible for low biodegradability and degradation rates of WAS (Li and Noike, 1992). Aside from the benefits already mentioned, hydraulic retention time (HRT) of digesters can also be reduced (Graja et al., 2005; Pérez-Elvira and Fdz-Polanco, 2012).

The assessment of thermal hydrolysis pretreatment effects on the AD of sludge, as well as the influence of decreasing the HRT of digesters in such conditions, can be done not only through regular monitoring of physicochemical parameters. Modeling is a powerful tool to provide additional information about biological processes, improving the understanding of the system, the formulation and validation of hypotheses and being able to predict system's performance (Donoso-Bravo et al., 2011a). Among the wide collection of AD models developed in the last decades, IWA's Anaerobic Digestion Model No. 1 (ADM1) is a structured and more complete approach, embracing several biochemical steps, as well as physicochemical phenomena (Batstone et al., 2002). It has been applied to the AD of several types of waste (Blumensaat and Keller, 2005; Galí et al., 2009; Mairet et al., 2011) and has potential for predicting effects of sludge pretreatments on AD (Souza et al., 2013), including thermal pretreatment (Phothilangka et al., 2008; Ramirez et al., 2009).

This study aimed to evaluate the effects of thermal pretreatment on the AD of sewage sludge, including the possibility of reducing HRT of digesters. The ADM1 was calibrated using batch tests data and employed as a tool for assessing the behavior of three continuous digesters, two of them fed with a mixture of raw PS and thermally pretreated WAS at different HRTs, and one used as a control and fed with a mixture of raw PS and raw WAS.

Table 1
Average waste characteristics.

		S1	S2
Composition	(gVS/gVS)	PS (50%) + TPWAS (50%)	PS (50%) + RWAS (50%)
pH	–	6.09 ± 0.07	6.38 ± 0.14
COD	($gO_2.L^{-1}$)	60.17 ± 2.02	62.00 ± 2.65
COD(s)[a]	($gO_2.L^{-1}$)	15.46 ± 4.74	5.50 ± 2.68
TS	($g.L^{-1}$)	57.12 ± 4.73	59.79 ± 4.98
VS	($g.L^{-1}$)	37.75 ± 2.35	40.22 ± 1.69
TKN	($gN.L^{-1}$)	2.71 ± 0.13	2.84 ± 0.20
TKN(s)[a]	($gN.L^{-1}$)	1.27 ± 0.03	0.34 ± 0.11
NH_4^+-N	($gN.L^{-1}$)	0.31 ± 0.03	0.15 ± 0.1
Proteins	(% bCOD)[b]	40	40
Carbohydrates	(% bCOD)[b]	30	30
Lipids	(% bCOD)[b]	30	30

TS, total solids; VS, volatile solids; TKN, total Kjeldahl nitrogen.
[a] Soluble fraction.
[b] Percentage of the biodegradable COD.

2. Methods

2.1. Waste characteristics

PS and WAS were obtained from the WWTP of Valladolid, Spain. Both were concentrated and mixed at a 50/50% ratio (gVS/gVS), with a final feeding concentration of approximately 40 $gVS.L^{-1}$. The procedure and VS feeding concentrations were the same regardless of whether WAS was pretreated or not. As a result, two types of substrate were obtained: S1, consisting of a mixture of PS and thermally pretreated WAS (TPWAS); and S2, consisting of a mixture of PS and raw WAS (RWAS). S1 and S2 were characterized through systematic monitoring of the digesters' feeding for one month, and average parameter values are shown in Table 1.

2.2. Continuous digesters and thermal pretreatment

Three identical 200-L digesters (A, B and C) were operated at 35 °C to treat sludge from the WWTP. Digesters A and B were fed with substrate S1, and digester C was kept as a control and fed with substrate S2 (Table 1). Digesters A and C were operated at a HRT of 20 days, while digester B was operated at the reduced HRT of 10 days. WAS was concentrated until 12–14% TS using a commercial centrifuge and then thermally pretreated in a Continuous Thermal Hydrolysis (CTH) industrial prototype operating with HRT of 40 min, temperature of 170 °C and pressure of 7.6 bar followed by steam explosion to atmospheric pressure. The main elements of the CHT prototype were preheater receiving steam from the flash, reactor with direct injection of steam at 10 bar and flash tank at atmospheric pressure. An overview of the experimental set-up is presented in Fig. 1.

Digesters were operated in three distinct phases, amounting for approximately 160 days of operation. Phase I consisted of a startup period of 50 days, for which simulations were not done, due to the instability of the reactor in the period. Phase II regarded the stable operation of the digesters, for approximately 80 days, with a feeding substrate of 40 $gVS.L^{-1}$, both for S1 (digesters A and B) and S2 (digester C). The final 30-day period was defined as phase III, in

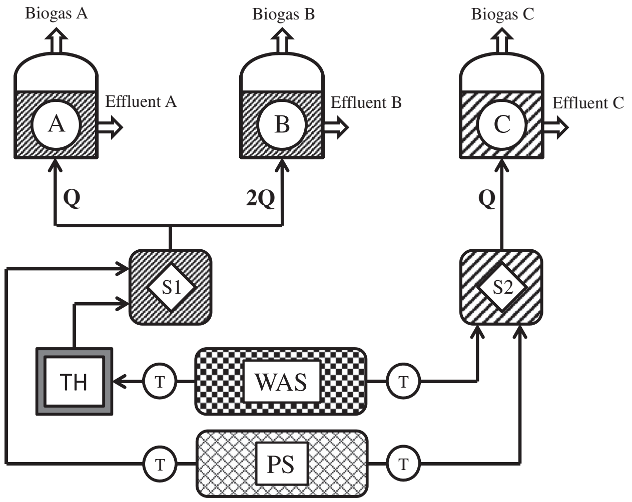

Fig. 1. Overview of the experimental set-up. PS: primary sludge; WAS: waste activated sludge; T, thickening; TH, thermal hydrolysis; S1, substrate type 1; S2, substrate type 2; Q, flow rate.

which the concentration of the feeding was increased to 55 gVS.L^{-1}. To eliminate punctual variability, as well as noise in the simulations, and for better comparison with experimental results from the digesters, a moving average considering a factor of 3 days was applied to inlet and outlet data.

2.3. Batch tests

Biochemical methane potential (BMP) tests were carried out in order to assess the sludge biodegradability and to provide data for model calibration. This was performed in three different series, each representing the current situation of digesters A, B and C, by combining the mixed sludge fed to each digester (substrate) with the corresponding effluent digested sludge (inoculum). This procedure was done for three timed samples collected throughout one month in phase II, and average results were used as the data source for further calibration.

All tests were made in triplicate at mesophilic conditions in a thermostatic room (35.1 ± 0.3 °C) with constant mixing in a shaker desk. The methodology used was the one suggested by Angelidaki et al. (2009). The substrate/inoculum ratio (S/I) used was 0.5 gVS.(gVS)$^{-1}$, as recommended by Neves et al. (2004). A control test without substrate was included in order to account for the methanogenic activity of the inoculum. All the assays were finished when the methane production was below 5% of the total cumulative production.

The biogas volume was monitored by periodic measurements of the headspace pressure by a manually pressure transmitter (IFM, PN5007, range 1 bar), and was expressed as methane yield (mL CH_4.(gVS$_{added}$)$^{-1}$), under standard temperature and pressure conditions (0 °C, 1 atm).

2.4. Analytical methods

Unless specified otherwise, all analyses were performed in agreement with the *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 2005). Carbohydrates (as glucose) were measured according to Dubois et al. (1956), and lipids were determined using the Soxhlet extraction method. Proteins were calculated using NH_4^+ and TKN data (Girault et al., 2012). Biogas composition was measured by gas chromatography (Varian CP-3800 CG) using helium as carrier gas.

2.5. Model implementation

The ADM1 was implemented following the guidelines of Batstone et al. (2002), and modifications proposed by Rosén and Jeppsson (2006), using Matlab/Simulink®. The disintegration and hydrolysis parameters contained in the ADM1 (k_{dis}, k_{hydch}, k_{hydpr} and k_{hydli}) were estimated for each digester by minimizing a least-square cost-function using data obtained in BMP tests (Section 2.3), as proposed by Souza et al. (2013). The remaining parameters were set according to Batstone et al. (2002). For model inputs, COD was fractioned considering substrate characterization (Table 1), following the procedures described by Souza et al. (2013). Biodegradable and inert COD fractions were defined according to the biodegradability obtained in BMP tests.

COD corresponding to biomass of the seven microbial populations contained in the ADM1 (X_{su}, X_{aa}, X_{fa}, X_{c4}, X_{pro}, X_{ac}, X_{h2}) were defined for BMP tests by performing a continuous simulation during a large period, starting with low concentrations of biomass and feeding the model with the same substrate as applied to the batch tests, until each biomass variable stabilized, as done by Girault et al. (2012), representing thus an overall proportion of microbial communities present in the inoculum. The same procedure was applied for simulating the continuous digesters.

With the set of hydrolysis parameters estimated for each digester, continuous simulations were performed considering variations in the flow rate and adjusting proportionately the COD fractioning to the inlet concentrations during operation. Simulations were then compared with experimental data to assess the effects of thermal pretreatment and HRT reduction on the digesters.

3. Results and discussion

3.1. Digesters performance

Table 2 shows the performance of digesters A, B and C considering the main parameters, in phases II and III. Phase I was not evaluated since it consisted of a startup phase, and comparison was not possible under startup conditions.

Throughout the 80 days of operation in phase II, even though variations in the parameters were observed mainly due to feeding variability, in overall the average results were in accordance to the expected. CH_4 production was the lowest for digester C, presented a small improvement for digester A and a significant improvement for digester B. When compared to the control digester (C), digester A showed a 17% higher CH_4 production in phase II. This increase may appear low at first, but it must be considered that the thermal pretreatment was applied only to the WAS fraction of the substrate and, although a CH_4 production increase of 33% was reported in similar conditions (Pérez-Elvira and Fdz-Polanco, 2012), differences in the composition of PS and WAS in the mixed sludge, as well as operational variability may have caused the lower production. A much more significant CH_4 production in phase II was obtained in digester B, though, accounting for an average 82% enhancement when compared to the control. This shows the potential of thermal hydrolysis not only in increasing biodegradability and methane productivity of WAS, but also in allowing lower HRTs to be employed, and consequently reducing the size of digesters in full-scale applications.

Phase III showed a similar behavior regarding the comparison of digester B with the control (Table 2), but CH_4 production was almost the same for digesters A and C. In this phase, operation was much more unstable due to the increase in feeding concentration and operational problems, as discussed further in Section 3.3, and a sharp drop in performance was observed for digesters A and B. Therefore, results were affected by such variations, hindering the evaluation based on average parameters.

Table 2
Average performance of digesters A, B and C in phases II and III.

	Phase II			Phase III		
	A	B	C	A	B	C
CH_4 production (L.d^{-1})	104 ± 17	162 ± 29	89 ± 20	120 ± 25	219 ± 57	117 ± 17
Effluent COD (g O_2.L^{-1})	28 ± 2	30 ± 2	33 ± 3	29 ± 2	32 ± 2	32 ± 3
Effluent NH_4^+ (g N.L^{-1})	1.4 ± 0.1	1.3 ± 0.1	1.0 ± 0.2	1.6 ± 0.2	1.6 ± 0.2	1.3 ± 0.1

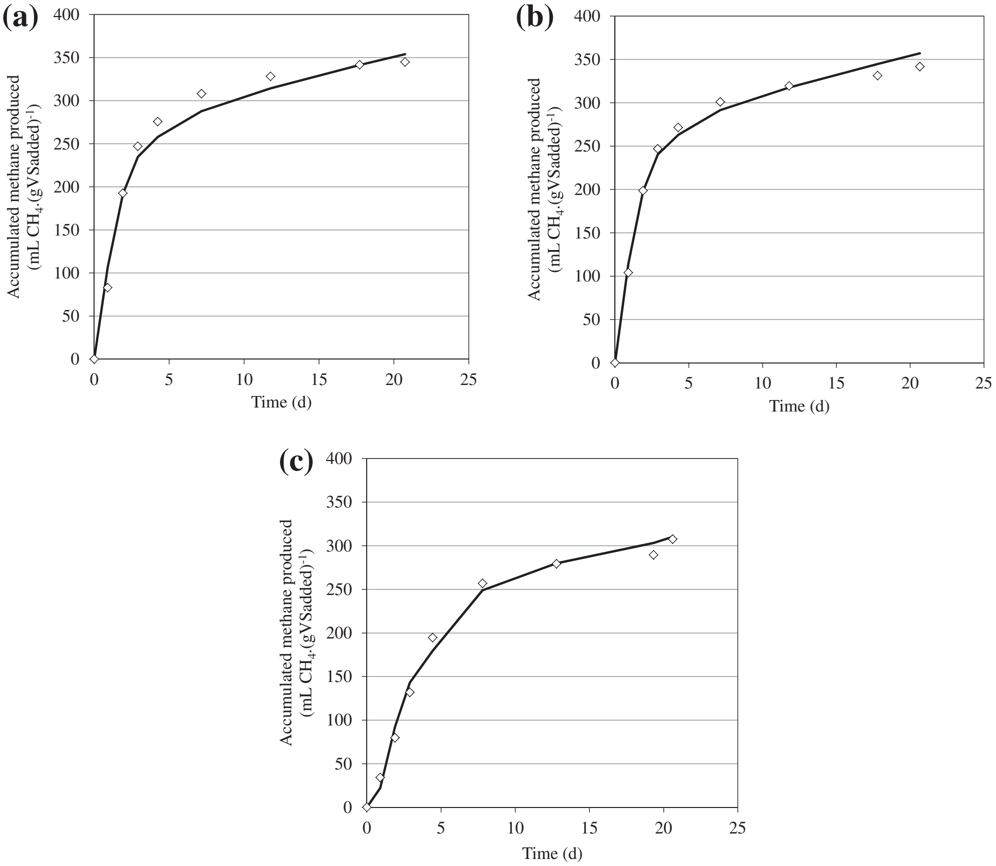

Fig. 2. Experimental results of the BMP tests (◇) and model fit (continuous line) after calibration regarding ADM1 disintegration and hydrolysis coefficients for digesters A (a), B (b) and C (c).

Effluent COD did not present sharp variations, and remained averagely in the range of 28–33 g O_2. L^{-1} for all digesters, according to Table 2. However, effluent ammonium presented itself in different levels, depending on the type of substrate fed to the digesters, with higher values for digesters A and B, fed with TPWAS. Indeed, thermal pretreatment is responsible for an increase in ammonium concentrations during anaerobic digestion, as also reported by Photilangka et al. (2008), and this effect was even more pronounced in phase III. More detailed discussion about the behavior of the digesters in specific periods is presented in Section 3.3, coupled with modeling analyses.

3.2. Calibration of disintegration and hydrolysis coefficients

The differences in CH_4 productivity given by the results of BMP tests are clearly visible in Fig. 2. Results corresponding to conditions applied to digester C (Fig. 2c) were not much higher than 300 mL CH_4.$(gVS_{added})^{-1}$, while tests corresponding to digesters A and B (Fig. 2a and 2b, respectively) reached 350 mL CH_4.$(gVS_{added})^{-1}$. Regarding anaerobic biodegradability, BMP tests resulted in values of 63.4%, 61.4% and 53.7%, for samples corresponding to digesters A, B and C, respectively. Moreover, the initial kinetics of CH_4 production for digesters A and B were evidently faster than for digester C. This confirms the potential of thermal pretreatment in not only increasing the degradation extent of sludge in anaerobic digestion, but also in improving the degradation rates. When comparing results for digesters A and B, though, no clear difference can be observed between the data points, indicating that the HRT did not affect the inoculum specific CH_4 productivity.

Table 3
Calibrated disintegration and hydrolysis coefficients for digesters A, B and C.

Digester	A	B	C
Substrate type	S1	S1	S2
HRT (d)	20	10	20
k_{dis} (d^{-1})	2.57	1.62	0.56
k_{hydch} (d^{-1})	0.66	0.78	0.51
k_{hydpr} (d^{-1})	0.78	0.79	0.44
k_{hydli} (d^{-1})	0.88	0.84	0.42
R^2	0.989	0.994	0.992

Calibration for ADM1 disintegration and hydrolysis coefficients produced optimum curves with good fits for experimental data, as can be seen in Fig. 2. Calibrated coefficients that generated the optimum fits for each case are shown in Table 3. Two separate behaviors could be inferred by the resulting coefficients: one associated to the disintegration coefficient k_{dis}, and the other related to the hydrolysis coefficients k_{hydch}, k_{hydpr} and k_{hydli} as a group. The coefficient k_{dis} was the most affected when comparing calibration results between the different digesters, as shown in Table 3. Fivefold and threefold increases for this coefficient were obtained, when comparing digesters A and B with digester C, respectively. Increases for k_{hydch}, k_{hydpr} and k_{hydli} were less representative in both cases, though.

The sharp increase of k_{dis} is in accordance to the expected effect caused by the pretreatment on the ADM1 disintegration step. Higher values of this coefficient represent that the destruction of bigger and complex particles is enhanced by the applied pretreatment, increasing the kinetics of this specific step. Similarly, Souza et al. (2013) obtained an increase from 0.24 to 5.60 d^{-1} in the coefficient k_{dis} when a low-thermal pretreatment was applied to sewage WAS. To describe properly the anaerobic digestion of thermally pretreated WAS, Photilangka et al. (2008) had to change k_{dis} from 0.25 to 1.5, which is also in accordance with the obtained results. Regarding calibration for raw WAS, Batstone et al. (2008) and Donoso-Bravo et al. (2010) obtained single hydrolysis coefficients of 0.15–0.25 d^{-1}. In the case of the present study, coefficients in the range of 0.42–0.56 d^{-1} were obtained for digester C (Table 3), and those values are higher than the reported ones because in this study a mixture of PS and WAS was fed to the tests, therefore presenting faster kinetics due to the more biodegradable nature of the feeding.

The three hydrolysis coefficients, k_{hydch}, k_{hydpr} and k_{hydli}, varied less significantly among digesters and among themselves, with all three being in the same range for each case. Due to this characteristic, kinetics of the initial steps of the anaerobic digestion process in the ADM1 in this study presented themselves in two main stages for digesters A and B: a fast disintegration stage and a subsequent slow hydrolysis stage. In this sense, the numerical difference of k_{dis} between digesters A and B (Table 3) may not be important, since both represent non-limiting steps, with probably no significant physical meaning regarding their difference. For digester C, though, both disintegration and hydrolysis steps may play an important role in modeling, since they are all in the same range.

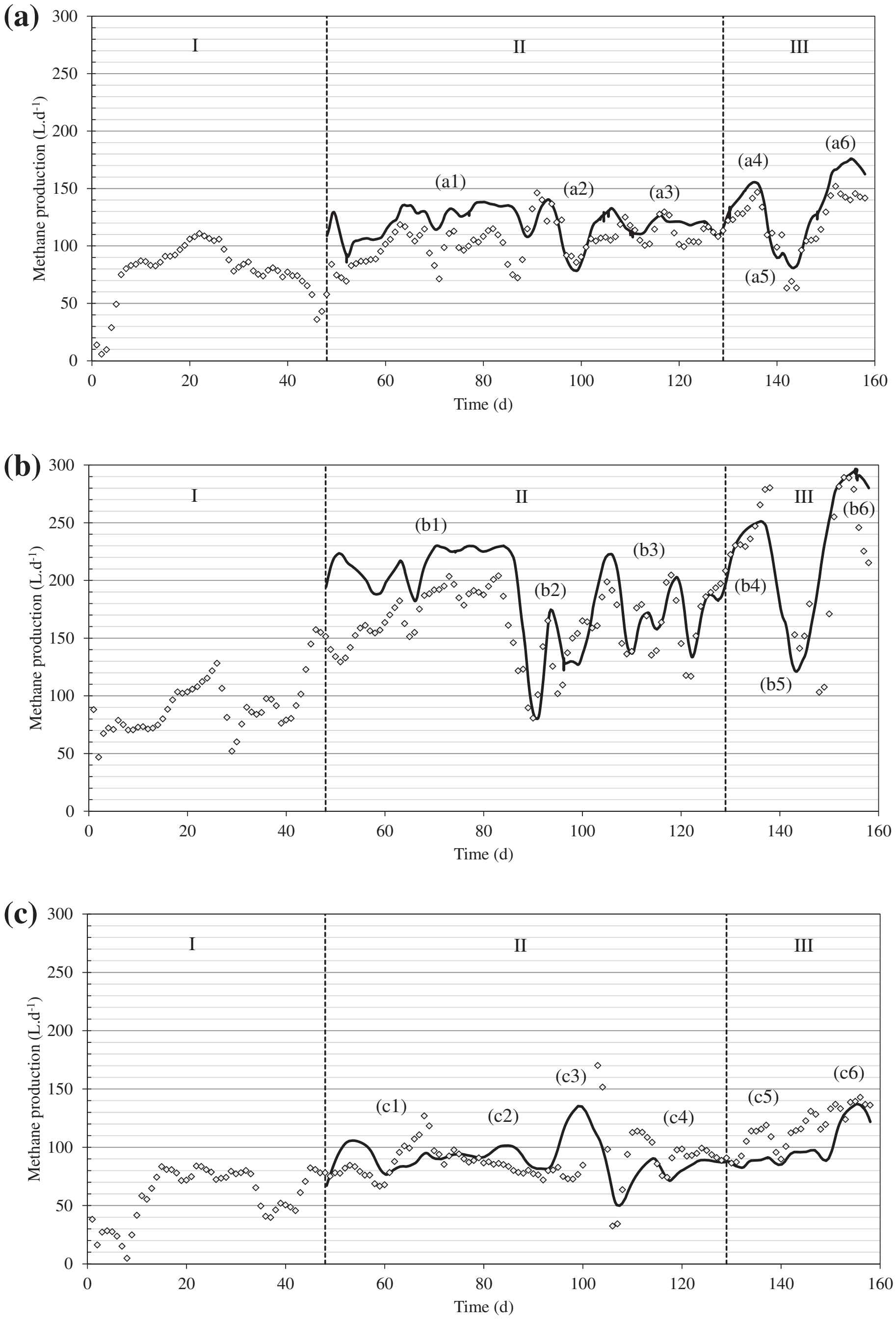

Fig. 3. Validation of the calibrated model with respect to methane production, using data from digesters A (a), B (b) and C (c): (◇) experimental data, (–) simulation. Discontinuous vertical lines represent changes in operational phase, and codes in parenthesis are used to name different regions of the graphics for enhanced discussion.

3.3. Validation using continuous digesters data

The experimental CH_4 production throughout the operation of digesters A, B and C, as well as the simulations using the calibrated model in each case, are presented in Fig. 3. Simulations followed really close the behavior of the digesters in some regions of the graphics, while in others some deviations were observed, as further discussed. Due to the instability of the startup phase (phase I), simulations are not presented in the graphics or discussed for this phase.

For digesters A and B, the initial regions of phase II, (a1) and (b1), were characterized by an overestimation of the CH_4 production, as can be seen in Fig. 3a and b. A similar, but minor, effect was also observed for digester C, in the region (c1) of Fig. 3c, but embracing model underestimation as well. The observed simulation results for the mentioned regions may be explained by the fact that those regions are immediately after the startup period of the digesters and, while some experimental instability were occurring in those regions, predictions were more optimistic for CH_4 production (mainly for digesters A and B), causing the differences. In this sense, it can be inferred that the model recovered faster from the instabilities of phase I than the digesters themselves. For digester C, region (c1) shows instability as well, which was not properly followed by the simulations, resulting in under and overestimation in this specific period.

After the initial periods of phase II, simulations predicted the behavior of the digesters with higher accuracy, which is evident mainly in regions (a3), (b3), (c2) and (c4) shown in Fig. 3. Predictions had good quality even when sharp experimental variations in CH_4 production were observed, such as the ones contained in regions (a2), (b2) and, in a lesser degree, (c3). The peaks and drops were related to the influent COD that presented a high variability in those regions and, since the same variations were fed as COD to the model, predictions also followed the tendencies, which showed good model robustness in this sense.

Phase III presented an increase in CH_4 production for all digesters, due to increased feeding concentrations, and consequently higher organic loading rates. The improvement in CH_4 production was sustained during the whole phase for digester C, as shown in Fig. 3, but the same was not true for digesters A and B, which suffered a sharp drop in performance after approximately one week of operation in this phase, with a later recovery at the end of the period. Nonetheless, model predictions followed correctly this behavior, representing well the peaks (regions (a4), (a6), (b4) and (b6)) and drops of performance (regions (a5) and (b5)). Digester C responded faster to the increase in organic loading rates than the model, as can be seen in region (c5), and simulations only reached the higher levels of CH_4 production at the end of phase III (region (c6)).

The instability observed in phase III for digesters A and B were not caused by variations in the inlet COD as happened punctually in phase II, but the sharp drop in CH_4 production resulted from operational problems with the feeding, which was done with reduced flow rates for some days, decreasing CH_4 production in the period. Since the model takes into account the flow rates applied to the digesters, this phenomenon was accurately followed in the simulations. Digester C did not present this operational problem; therefore such a drop in performance was not detected.

Concerning the ammonium concentrations, the model was able to predict this parameter accurately as well. The simulated average ammonium concentrations in phase II were 1.49, 1.39 and 0.91 g $N.L^{-1}$ for digesters A, B and C, respectively. During phase III, those concentrations were 1.64, 1.69 and 1.15 g $N.L^{-1}$, in the same order of digesters. When compared to the average experimental data for this parameter, presented in Table 2, simulated values presented good performance, with average differences not higher than 12%. This indicated that the model was also able to predict the effect of thermal pretreatment on the increase of ammonium in the effluent.

In overall, it can be observed in Fig. 3 that the differences in operation conditions for each digester, regarding the application of pretreatment and reduction of HRT, were correctly represented by the model. Increases in the values mainly of the disintegration coefficients of the ADM1, as well as the solubilization of COD promoted by the thermal pretreatment, coupled to the increased flow rate applied to the model (for digester B only) were assumed to be responsible for those distinct behaviors. The changes in CH_4 production levels are evident when comparing digester A (Fig. 3a) and C (Fig. 3c), and even more when considering the high CH_4 production of digester B (Fig. 3b), and the simulations were able to follow closely those tendencies. In respect to the accuracy of the model considering the average CH_4 production, Table 4 shows the high quality of the predictions in both phases, with average overestimations (or underestimations) lower than 15%, and as low as 1.1%. This clearly demonstrates that the procedures and considerations used to perform the simulations with the calibrated model were successful in predicting the behavior of the three digesters.

3.4. Thermal pretreatment and HRT assessment

The effect of the thermal pretreatment and changes in HRT on the performance of digesters A, B and C were assessed using the accumulated CH_4 production curves throughout the whole operation period (not considering phase I), as shown in Fig. 4, both for experimental data and simulation results. This was done to account for the global differences between each digester, regardless of punctual variations of CH_4 production, and a similar approach was also reported by Photilangka et al. (2008).

It can be observed in Fig. 4a that the global accumulated CH_4 production of digester A suffered a small increase of only 12%, when compared to the control digester (C). As also discussed in Section 3.1, this improvement is lower than expected, since other studies obtained increases in CH_4 production of 20–30% when treating mixed sludge (Barjenbruch and Kopplow, 2003; Pérez-Elvira and Fdz-Polanco, 2012), although there are reports of lower increases in the range of 10–20% (Haug et al., 1978; Donoso-Bravo et al., 2011b), which depend on experimental conditions, variability of results and performance of digesters in each case. The improvement in CH_4 production for digester A was more optimistic

Table 4

Comparison between experimental and simulated average methane production for the three digesters in phases II and III, as well as model's overestimation in each case.

	Phase II			Phase III		
	A	B	C	A	B	C
Experimental CH_4 production ($L.d^{-1}$)	104 ± 17	162 ± 29	89 ± 20	120 ± 25	219 ± 57	117 ± 17
Simulated CH_4 production ($L.d^{-1}$)	119 ± 14	185 ± 36	90 ± 16	134 ± 29	233 ± 58	101 ± 18
Overestimation (%)	14.4	14.2	1.1	11.7	6.4	−13.7[a]

[a] Negative values mean that the simulation underestimated the parameter.

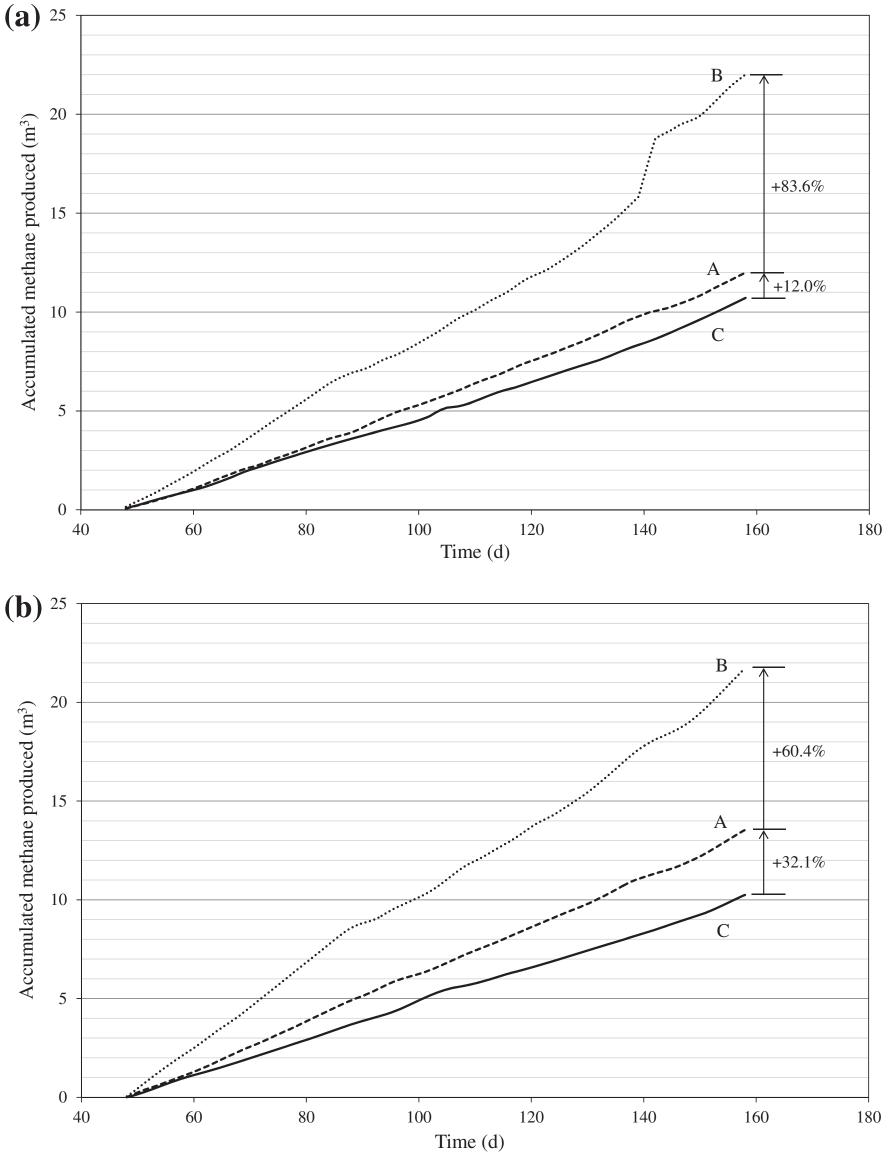

Fig. 4. Experimental (a) and simulated (b) methane accumulated throughout the operation period (not considering phase I) for digesters A (- - -), B (···) and C (—). Upward arrows represent the improvement in methane production between each pair of digesters.

according to simulation results (Fig. 4b), accounting for an enhancement of 32.1% when compared to digester C, since overestimation was evident in some operation periods, such as the one depicted in region (a1) (Fig. 3a).

When the accumulated CH_4 production of digester B is compared with digester A, increases in this parameter were 83.6% and 60.4%, for experimental data and simulation results, respectively (Fig. 4). Those differences were affected by the results of digester A, discussed above. Nonetheless, when digester B is compared with the control, differences in CH_4 accumulation were accurately represented by the simulations, accounting for an enhancement of 95.6% and 92.5%, for experimental data and simulations results, respectively. These results show that reducing the HRT from 20 to 10 days had a great effect on CH_4 production, and digester B could sustain such an increase in organic load throughout the operation period. Although the flow rate is doubled in this case, CH_4 production does not double as well, due to the fact that the anaerobic digestion process is limited under such HRT and organic load, and the specific CH_4 yield ($L.(gVS_{fed})^{-1}$) is reduced. In this context, Pérez-Elvira and Fdz-Polanco (2012) obtained an increase in biogas production of 71.4% when reducing the HRT from 17 to 9 days in digesters fed with a substrate similar to S1, with a coupled decrease in the specific biogas yield from 652 to 607 $L.(gVS_{fed})^{-1}$. The reported increase in biogas production is similar to both the experimental (83.6%) and simulated (60.4%) increases in CH_4 production when comparing digesters A and B.

Considering the final amount of CH_4 produced in each digester, Table 5 shows that the model presented extremely high accuracy for digesters B and C, with a slight underestimation of the accumulated CH_4. Simulations related to digester A, however, presented

Table 5
Comparison between experimental and simulated total methane accumulation throughout operation in phases II and III for each digester, and overestimation of the predictions.

	A	B	C
Experimental CH_4 accumulation (m^3)	11.9	22.0	10.7
Simulated CH_4 accumulation (m^3)	13.5	21.7	10.2
Overestimation (%)	13.4	−1.4[a]	−4.7[a]

[a] Negative values means that the simulation underestimated the parameter.

less quality in this regard, with an overestimation of 13.4%. Nevertheless, those are acceptable levels of accuracy taking into account the variability of operation. Therefore, results demonstrate the feasibility and usefulness of using the ADM1 under the studied conditions to predict the effects of both a thermal hydrolysis pretreatment and the manipulation of HRT in the operation of sludge digesters.

4. Conclusions

The results provided by the present study demonstrated the feasibility and usefulness of using the ADM1 to predict and assess the effects of both thermal pretreatment and changes in HRT in the performance of sewage sludge digesters. The calibration results, obtained via BMP assays, showed an important increase in the disintegration step, caused by the pretreatment, and the validation of the calibrated model presented good accuracy even considering operational variability, with under/overestimation of both average and accumulated CH_4 production lower than 15% in all cases.

Acknowledgements

This research group is “Grupo de Excelencia GR76 de la Junta de Castilla y León” and member of the Consolider_Novedar framework (Project CSD2007-00055, Programa Ingenio 2010, Spanish Ministry of Education and Science). The experimental data of CTH were obtained within the project SostCO2 led by Aguas de Barcelona (Aqualogy). The authors would like to thank Guzmán García for his contribution.

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