# Hydrothermal hydrolysis of triglycerides: Tunable and intensified production of diglycerides, monoglycerides, and fatty acids

Enkeledo Menalla , Juan García Serna, Danilo Cantero , María José Cocero [*]

*Pressure Technologies group (PressTech), The Institute of Bioeconomy at the University of Valladolid (BioEcoUVa), Department of Chemical Engineering and Environmental Technology, School of Industrial Engineering. University of Valladolid, 47011 Valladolid, Spain*

ARTICLE INFO

ABSTRACT

This study focuses on utilizing subcritical and supercritical water technology to produce intensive and selective diglycerides, monoglycerides, and fatty acids. The water properties can be easily modified by adjusting pressure and temperature, which promotes an improving solubility of the triglycerides in water and a selective production of glycerides. Triacetin and sunflower oil were used as models for short and long-chain components, exploring a range of temperatures (250 to 400 °C), pressures (22.0 to 25.0 MPa), and reaction times (0.7 to 29 s). A conversion of 98.5 % of sunflower oil is reached at 375 °C and 25.0 MPa in 29 s. The resulting products are 16.3 % diglycerides, 27.9 % monoglycerides, 48.9 % fatty acids, and 5.3 % glycerol. On the other hand, only 13 % of the oil is hydrolyzed at 300 °C, 22.0 MPa, with a reaction time of 23.6 s. The main product at this condition was fatty acids with a yield of 3.7 %. Furthermore, a kinetic model was developed to obtain comprehensive kinetic parameters for both raw materials to evaluate their reactivity during hydrolysis. This study provides valuable insights into the hydrolysis kinetics and the most promising conditions to make valuable products like fatty acids, mono and diglycerides, and glycerol.

## 1. Introduction

The global demand for sustainable and efficient methods of producing valuable lipid compounds, such as diglycerides, monoglycerides, fatty acids, and glycerol, has significantly increased due to their applications in the cosmetics and food industries. It is estimated that by 2030, consumption could reach 14.28 billion USD[1–3]. Triglycerides, found abundantly in natural fats and oils, present a promising source for these lipids. Yet, their conversion into targeted products poses a substantial challenge [4]. Diglycerides and monoglycerides, long-established emulsifiers in the food industry, improve texture, stability, and shelf life. These compounds prevent ingredient separation, enhancing the quality of baked goods and the texture and volume of bread [5]. Additionally, they serve as carriers for flavors, colors, and nutrients within food products. Beyond the realm of food production, these substances find utility in pharmaceuticals, acting as effective drug delivery systems [6] and components in pharmaceutical formulations [7]. Furthermore, their application extends to the cosmetic industry [8], illustrating their versatile role in different domains. Triglycerides are also used to make biodiesel, commonly triglycerides are hydrolyzed releasing fatty acids that are subsequently *trans*-esterified [9,10].

Several methods are used for producing diglycerides, monoglycerides, and fatty acids. Lipolysis processes stand as a fundamental approach, utilizing enzymatic action to hydrolyze triglycerides, yielding glycerol and fatty acids [11]. Acid-catalyzed or alkaline hydrolysis can be employed to break down triglycerides into the same products [12]. Also, triglycerides can be transesterified using an alcohol and a catalyst to yield glycerol and fatty acid esters [13]. Partial hydrogenation processes, a widely utilized method, chemically convert unsaturated fatty acids into monounsaturated or saturated fatty acids, often yielding diglycerides as intermediates [14].

Hydrolysis is a simple and efficient way of diglycerides, monoglycerides, and free fatty acids (FFA) from triglycerides. The reaction takes place by breaking down the ester bonds present in triglyceride molecules [15]. Rodrigues claims that the yield of transesterification is 90 % in 10 h of reaction time [15]. Also, the conversion of fatty acids is 95 % in the same time using hydrolysis. Sub and supercritical water (SCW) hydrolysis is a promising technology to break down glycerides because the medium offers advantages from its unique properties. Firstly, the reaction rate is significantly accelerated under the high temperature and pressure conditions of SCW, leading to faster conversion of esters into fatty acids and glycerol. For example, the enzymatic

hydrolysis of cooking oil utilizing lipase enzyme at 30 °C and pH 7 exhibits a 92 % Free Fatty Acid (FFA) production efficiency over 30 h [16]. Alternatively, 95 % of FFA can be produced in 2 h by running subcritical water hydrolysis in a batch reactor at 250 °C [17].

Water experiments fascinating properties changes when its temperature is change from ambient to supercritical state. For example, the dielectric constant of water decreases as density does and rising temperature. The dielectric constant of water takes values of single digits at SCW conditions, which promotes the solubility of non-polar compound as triglycerides and its reaction products. This improved solubility facilitates a better mass transfer and increased reaction yields [18]. Importantly, this process avoids the limitations associated with enzymatic hydrolysis, eliminating the need for specific enzymes and circumventing challenges related to pH, temperature, and substrate concentration. Additionally, as SCW itself can act as a catalyst [19], there is no requirement for external catalytic agents which simplifies the process. This method aligns with the principles of green chemistry, as it removes the use of harsh chemicals and produces fewer byproducts, contributing to a more environmentally friendly approach to chemical synthesis. Another important factor is that our research team has vast experience working with sub-supercritical biomass hydrolysis. This technology has given excellent results for the fractionation of lignocellulosic biomass used in different fields: hydrolysis of sugarcane [20], hydrolysis of cellulose and beet pulp [212223], transformation of fructose into lactic acid [24] depolymerization of lignin [25,26] and generating new products from grape seeds [27].

Significant advancements in the elucidation of the triglyceride hydrolysis process have been attributed to the research efforts of Savage and Saka. Savage's work in a batch reactor, conducted at 300 °C for 60 min under pressure, achieved complete conversion of ethyl oleate to produce oleic acid [28]. Furthermore, Savage utilized oleic acid as a precursor in the subsequent step to synthesize biodiesel [29]. Saka, on the other hand, conducted research using rapeseed oil. A 90 % yield of fatty acids was obtained within 20 min of reaction time at 275 °C, 200 MPa, and a molar ratio of ¼ [30]. In another study, Saka obtained a 90 % yield of fatty acids within the same 20 min timeframe with a modified oil/water ratio of 1/1, at 320 °C and 20 MPa [19]. Both authors significantly contributed to our understanding of the intricate reaction mechanisms involved in triglyceride hydrolysis, shedding light on the fundamental processes and conditions that influence the conversion of oils to valuable fatty acids and biodiesel.

Additional research in the field of subcritical water hydrolysis has provided insights into ester hydrolysis. For instance, one study observed that 99 % of ethyl acetate undergoes hydrolysis at 350C and 25.0 MPa pressure within 3.5 min [31]. Another research focused on the hydrolysis of triglycerides, such as palm oil, resulting in the production of 86 % of fatty acids within 120 min at 250 °C in a batch reactor [32]. Moreover, soybean oil was examined, and it was found that 90 % of fatty acids were produced within 40 min at a temperature of 300C in a similar batch reactor setup [33].

Triacetin was selected as a model component in our scenario due to its straightforward synthesis, high purity, classification as a triglyceride, simplicity of structure, and nontoxic molecule [9,34]. It exemplifies the characteristics of shorter-chain triglycerides, making it an ideal candidate for simulating the hydrolysis process in a more controlled and understandable manner. The choice of triacetin, a compound well-studied for its ease of handling and availability in commercial quantities, ensures that our research can proceed with a well-defined and easily replicable model system. The simplicity of triacetin's kinetic model, which is nevertheless comprehensive, provides critical insights into reaction dynamics such as rates and activation energies, laying the groundwork for more complex studies. After that, triglycerides such as sunflower oil, can be used to present the entire picture and make the processes more realistic. Sunflower oil presents multiple ester linkages. This means a more complex structure and more fatty acid chain variations when you compare it with triacetin.

Another important aspect is separating the diglycerides, monoglycerides, and fatty acids. Pereda has studied the fractionation of glycerol acetates [35] and fatty acid and acyl glyceride esters[36] by supercritical $CO_2$, correlating the equilibrium data with GCA-EOS (Group Contribution and Association Equation of State). They provide the performance of a multi-stage countercurrent column. A raffinate product with up to 99.8 wt% monoglycerides can be obtained in a seven stages extraction column operated at 110 bar and temperatures between 310 K and 316 K, working with a solvent-to-feed ratio between 12 and 30 kg $CO_2$ / kg of oily substrate, respectively.

The objective of the research was the hydrolysis of triglycerides in continuous SCW reactors to yield fatty acids, monoglycerides, and diglycerides, with a focus on precise control of product yields. Triacetin served as a model compound molecule in our study, and we extended it to sunflower oil. The overarching objective is to develop a kinetic model that not only facilitates the design of reaction engineering processes but also enhances our understanding of the intricate mechanisms governing the hydrolysis of glycerides. Furthermore, a broader aim of the study was to gain comprehensive insights into the hydrolysis of ester bonds, thereby allowing extrapolation to the understanding of hydrolysis in complex polyester-containing biomass. Through this multi-faceted approach, the research aimed not only to elucidate the fundamental chemical reactions involved but also to facilitate a robust design methodology for reaction engineering in the context of biodiesel and emulsifier production.

## 2. Experimental work

### 2.1. Materials

Triacetin (lot number SHBN0219) and glycerol (0000198501) were purchased from Sigma Aldrich and the standards diacetin (Lot number 10227368) and monoacetin (Lot number Q12H088) were purchased from Alfa Aesar. Sunflower oil was procured from local stores from the brand "Koipe Sol." Distilled water from Elix 10 mA was used as the reaction medium to run the experiments. Solvent analysis for GC/MS: BSTFA (Lot number 102448727), pyridine (Lot number 102471057), and heptane (Lot number STBK0472) were purchased from Sigma Aldrich.

### 2.2. Supercritical water hydrolysis: The device

The continuous hydrolysis device, PHUn 1, is depicted in Fig. 1. PHUn 1 states for "Pressurized Hydrolysis Unit". This setup operates with a sudden expansion reactor (SER) designed to operate up to 400 °C and 30 MPa. The reactor is made of stainless steel 316L, and the connection between the hot water stream and the depressurization valve are ¼" Swagelok fittings. The outer diameter of the reactor is 6.35 mm (1/4 in.) and the wall thickness is 0.89 mm, its length varies from 0.07 m to 5.1 m based on the desired reaction time. The reactor is depressurized by a needle valve, which facilitates rapid cooling through the Joule-Thomson effect. The sudden depressurization enabled an immediate reduction in temperature from 400 to 150 °C, effectively preventing uncontrolled reactions. The manual needle valve employed was the 30VRMM4812-HT model from Autoclave Engineers. The unique combination of ultra-rapid heating and cooling, developed by our research group, offers detailed control over the hydrolysis process, optimizing product selectivity and efficiency [37,38].

The triglyceride suspension feed was placed in a 2-liter polypropylene (PP) tank. The pumping system includes a Dosapro Milton Roy MD140 membrane pump (P – 201), which conveys water at a maximum rate of 5 kg/h, and a Lewa EK1 piston pump (P – 101) used for pumping oil suspensions containing 10 % w/w oil at a rate of up to 2.6 kg/h. Both pumps are used to raise the pressure of water and oil suspensions to the operational operation pressure of 25 MPa. At the mixing point, the triglyceride suspension is mixed with a stream of hot
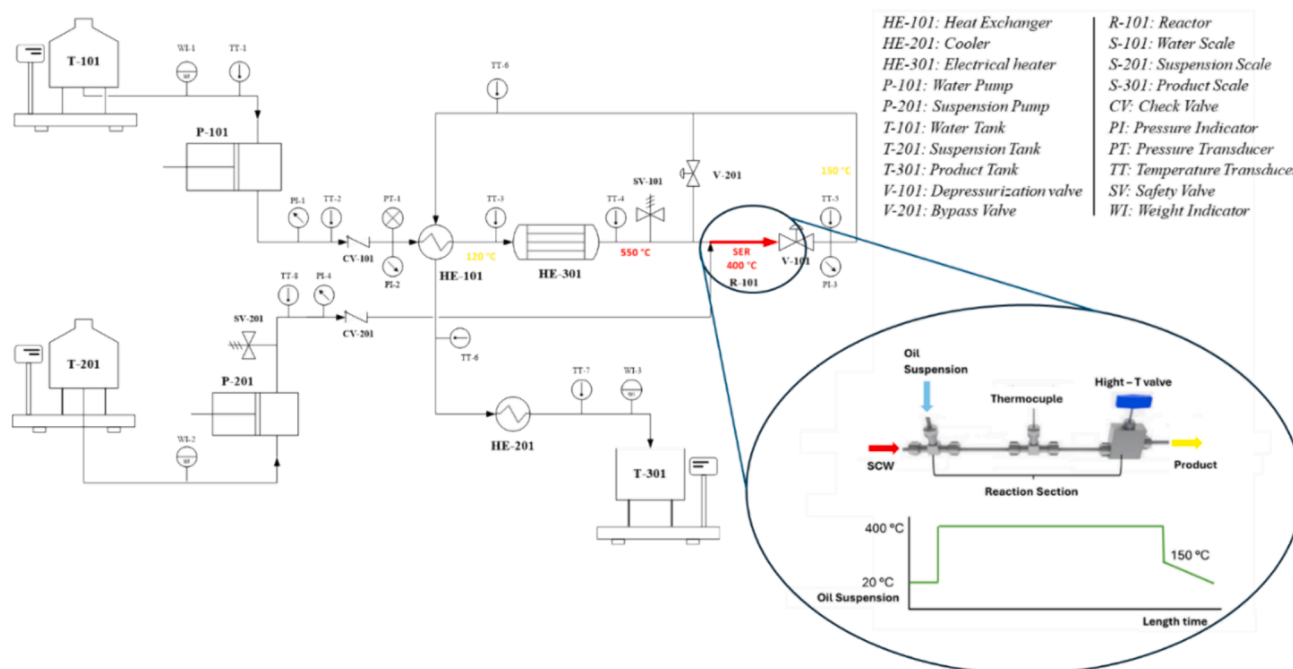
**Fig. 1.** PFD diagram of the continuous SCW pilot plant.

pressurized water, causing a fast heating of the triglycerides. The reactions start just after the mixing point. Modifying the reaction time involved adjusting both the length of the reactor and the total flow rate. Changing the reactor length requires bringing down the equipment and breaking the lines. However, utilizing the same reactor enables varying temperatures and pressures as needed without interrupting the operation.

The reactor operates by taking the heat from the supercritical water stream and is fully insulated with glass wool, which has a thickness ranging between 60 to 90 mm. For shorter reactor lengths, it adopts a linear configuration, with the thermocouple situated centrally within the reactor. In contrast, when the reactor is elongated, such as in the spiral shape with a length of 5.1 m, the thermocouple is placed at the end of the reactor just before entering the valve.

Through the utilization of continuous reactors, the extent of the hydrolysis reactions can be controlled with high precision ($\sim0.1$ s). This is because the reaction time can be precisely modified by changing the reactor volume. The use of high reaction temperature promotes fast reactions and the precise control of the reaction time prevents products degradation. Then, this combination allows high selectivity towards desired products. Also, the fast reactions allow process intensification to carry out the process in very compact reactors. Notably, there is no degradation of the raw material before its introduction into the high-temperature reactor. Moreover, the reaction can be swiftly halted within the timeframe of 0.1 to 1 ms using the depressurization valve, ensuring efficient process control and preventing undesired secondary reactions.

To achieve the desired reaction conditions, only water is initially pumped into the system from both pumps. Once these conditions (temperature and pressure) are reached and stabilized, the oil suspension is then introduced. Observation of color changes in the T-301 tank signals the need to replace the product containers to a clean and empty one. Subsequently, the balance is reset to zero, and product collection begins. The supercritical water stream is generated by pumping DI water through an in-line electrical heater (HE-301; 9 kW). This heater is an internal design of the PressTech team. Briefly, a 6 m Inconel coil is placed together with 3 resistances inside cast bronze.

Finally, there is a heat exchanger (HE-101) that serves to recover energy from the product stream. The product is finally cooled down to room temperature in a cooler represented as HE-201.

### 2.3. Experimental design

The experimental conditions were made thoughtfully to cover variations in water properties while also considering the alterations in the chemical and physical properties of triacetin/triglycerides, as well as the kinetic study of reaction temperatures and times. The conditions tested for both feedstocks were similar to correlate as much as possible the experimental information (see Table 1).

Five temperatures (250, 300, 375, 385, and 400 °C) at two pressures (22.0 and 25.0 MPa) were tested for triacetin. Those conditions were run in six different reactor lengths (6.9, 30, 40, 110, 200, and 230 cm), giving different reaction times. This comprehensive approach ensures the exploration of the full spectrum of factors influencing hydrolysis. The flow rates were set at 4.5 kg/h for supercritical water (SCW) and 1.6 kg/h for the sunflower oil suspension. The oil concentration in the tank is 10 % w/w, while in the reactor, it is 2.72 % w/w. The selection of a 2.72 % w/w concentration is based on achieving a balance between ensuring an adequate amount of oil, as it is completely soluble, and facilitating efficient mixing and interaction with SCW. A thermodynamic model is currently developing and is being discussed in detail in the forthcoming study. The same concentration is selected for sunflower oil to remove any concentration effect from the comparison between reagents.

Due to the limited solubility of sunflower oil under subcritical water

**Table 1**
Physical properties of water at the experimental conditions tested [39].

| Temperature (°C) | Pressure (MPa) | Density ($kg m^{-3}$) | Ionic Product ($pK_W$) | Dielectric Constant |
|---|---|---|---|---|
| 250 | 22.0 | 818.0 | 11.0 | 28.1 |
| 275 | 22.0 | 781.1 | 11.0 | 24.6 |
| 300 | 22.0 | 738.1 | 11.2 | 21.4 |
| 325 | 22.0 | 685.1 | 11.3 | 18.2 |
| 350 | 22.0 | 611.6 | 11.6 | 14.4 |
| 375 | 25.0 | 505.5 | 12.3 | 9.3 |
| 385 | 25.0 | 312.3 | 14.0 | 7.1 |
| 400 | 25.0 | 166.5 | 16.7 | 3.7 |

conditions, the temperature range and reaction times were increased to better understand the reaction. The experiments were conducted at 250, 275, 300, 325, 350, 375, and 400 °C. The reactor lengths were set at 9, 100, 110, 200, 230, 318, and 510 cm, and the pressure was 25.0 and 22.0 MPa. These modifications enabled us to collect more thorough information and insights about the hydrolysis reaction.

The reactor pressure was maintained at 22 MPa at subcritical water temperatures. On the other hand, the pressure was elevated to 25 MPa under SCW conditions. By employing a pressure of 25 MPa, a margin of safety is established to ensure that the system consistently operates within the supercritical phase boundaries, thereby optimizing the desired thermodynamic and kinetic parameters for the intended hydrolysis process.

### 2.4. Characterization of the product

The hydrolysis products were analyzed with different techniques to make a comprehensive evaluation of the process. Different methodologies were employed due to the nature if the products composition. Triacetin is a pure component, yielding diacetin, monoacetin, acetic acid, and glycerol as products. Diacetin, monoacetin, and glycerol can be readily detected using GC–MS due to their purity. On the other hand, the presence of a mixture of components from sunflower oil hydrolysis requires the use of more sophisticated techniques than GC–MS or HPLC. These methods are inadequate for determining diglycerides, triglycerides, and the total monoglyceride content. Although fatty acids can be individually determined using GC–MS or HPLC, it necessitates the creation of calibration curves for each fatty acid present in the products and the method get more complicated.

Conversely, an alternative ISO method (ISO 18395:2012) employs high-performance size-exclusion chromatography (HPSEC) with a GPC column to determine the collective quantities of tri-, di-, and mono-acylglycerols, as well as fatty acids and glycerol. This approach is straightforward, yielding distinct peaks for tri-, di-, and mono-acylglycerols, fatty acids, and glycerol, simplifying analysis. The following sections explain the techniques and procedures applied.

#### 2.4.1. Gas chromatography

A gas chromatograph equipped with an HP-5 ms capillary column (30 m x 0.25 mm x 0.25 μm, Agilent Technologies, USA) was utilized for the identification and quantification of triacetin, diacetin, monoacetin, and glycerol in the product mix. A quadrupole mass spectrometer detector (5977A, Agilent Technologies, USA) was used for data acquisition, with the equipment operating in a 1/50 split mode and helium as the carrier gas. The oven temperature was initially set at 120 °C, maintained for 10 min, with a 4-minute solvent delay to avoid pyridine detection. Compound identification leveraged the NIST spectrum library, with Agilent MassHunter software aiding in data analysis. BSTFA derivatization and pyridine silylation prepared the samples, with calibration curves for TA, DA, MA, and glycerol enabling quantification. Acetic acid and water quantities were deduced from the reaction mass balance, facilitating insights into the reaction mechanism and kinetic parameters.

#### 2.4.2. HPSEC (high-performance size-exclusion chromatography)

This technique was employed to detect triglycerides, diglycerides, monoglycerides, and fatty acids derived from sunflower oil. Utilizing a styrene–divinylbenzene co-polymer gel column, the mobile phase flowed at 0.8 ml/min, with a column and detector temperature maintained at 35 °C. Sample preparation involved dissolving 100 mg of the sample in 10 ml of THF, followed by a 15-minute homogenization and filtration through a 0.22 μm nylon filter. [40]. The amount of glycerol was determined using stoichiometry and gas chromatography with the upper paragraph's method.

#### 2.4.3. Total organic carbon

This technique was used to analyze the aqueous phase using Shimadzu TOC-VCSH. To conduct the analysis, 0.5 ml of the sample were placed into a 50-milliliter vial. Subsequently, water was added until the total volume reached 30 ml. This solution was placed on the equipment and the TOC 500 method was selected to run the analysis.

#### 2.4.4. Fourier-Transform infrared spectroscopy (FT-IR)

This technique was utilized to assess the structural changes in triglycerides before and after hydrolysis using Bruker Tensor 27. The recorded spectra were baseline-subtracted and normalized to the maximum peak intensity. Each processed spectrum was hereby a mean of 64 single scans. The sample was analyzed without further preparation.

#### 2.4.5. Lyophilizator telstar LyoQuest

Freeze drying was used to remove water from the product and be ready to analyze in GC–MS. The working conditions of the Lyophilizator are temperature −50 °C and pressure less than 0.1 mbar.

### 2.5. Kinetic model of triacetin and sunflower oil

The kinetic parameters were determined relying on the studies conducted by Minami – Saka [19], Milliren [33], and Savage [29] who also investigated the influence of fatty acids acting as autocatalysts. These reactions are shown in equation (3) to (6).

$$TG + H_2O \rightleftarrows DG + FFA \tag{1}$$

$$DG + H_2O \rightleftarrows MG + FFA \tag{2}$$

$$MG + H_2O \rightleftarrows G + FFA \tag{3}$$

$$TG + H_2O + FFA \rightleftarrows DG + 2FFA \tag{4}$$

$$DG + H_2O + FFA \rightleftarrows MG + 2FFA \tag{5}$$

$$MG + H_2O + FFA \rightleftarrows G + 2FFA \tag{6}$$

A simplified reaction rate approach is used to construct a kinetic model for the hydrolysis reactions. The rate of each reaction is proportional to the concentration of the reactants. The rate constants for each step are denoted as k0, k1, and k2 for the first, second, and third reactions, respectively. The rate equations can be written as shown in equations (5) to (10).

$$\frac{dC_{TG}}{dt} = (-k_0 C_{TG} C_{H_2O} + k_{0_{-1}} C_{DG} C_{FFA}) x C_{FFA} \tag{7}$$

$$\frac{dC_{DG}}{dt} = (k_0 C_{TG} C_{H_2O} - k_{0_{-1}} C_{DG} C_{FFA} - k_1 C_{DG} C_{H_2O} + k_{1_{-1}} C_{MG} C_{FFA}) x C_{FFA} \tag{8}$$

$$\frac{dC_{MG}}{dt} = (k_1 C_{DG} C_{H_2O} - k_{1_{-1}} C_{MG} C_{FFA} - k_2 C_{MG} C_{FFA} + k_{2_{-1}} C_G C_{FFA}) x C_{FFA} \tag{9}$$

$$\frac{dC_G}{dt} = (k_{2_{-1}} C_G C_{FFA} + k_2 C_{MG} C_{FFA}) x C_{FFA} \tag{10}$$

$$\frac{dC_{FFA}}{dt} = \begin{pmatrix} -k_{0_{-1}} C_{DG} C_{FFA} + k_0 C_{TG} C_{FFA} - k_{1_{-1}} C_{MG} C_{FFA} + k_1 C_{DG} C_{FFA} \\ -k_{2_{-1}} C_G C_{FFA} + k_2 C_{MG} C_{H_2O} \end{pmatrix} x C_{FFA} \tag{11}$$

$$\frac{dC_{H_2O}}{dt} = \begin{pmatrix} -k_0 C_{TG} C_{H_2O} + k_{0_{-1}} C_{DG} C_{FFA} - k_1 C_{DG} C_{H_2O} + k_{1_{-1}} C_{MG} C_{FFA} \\ -k_2 C_{MG} C_{H_2O} + k_{2_{-1}} C_G C_{FFA} \end{pmatrix} x C_{FFA} \tag{12}$$

The ODE system for the kinetic model is simple and was solved using

forward Euler's method implemented in cells of a Microsoft Excel datasheet. A fixed time step of 0.01 min was sufficient to solve the system with enough precision. The objective function (OF) was computed as the sum of the squares of the percentage error between the amounts of the components that were measured experimentally and determined numerically by simulation. The objective function was minimized using the Solver add-in fitting the ki ($k_0, k_{0_{-1}}, k_1, k_{1_{-1}}, k_2, k_{2_{-1}}$) of the different equations. Finally, the Arrhenius equation was used to determine the activation energy.

The same pathway of reactions and equations is employed for triacetin (TA), with analogous components to triglycerides (TG), where diglycerides (DG) are denoted as DA, monoglycerides (MG) as MA, and free fatty acids (FFA).

## 3. Results and discussion

### 3.1. Solubility characteristics of hydrolysis products

The products of triacetin hydrolysis, including glycerol (G), acetic acid (Hac), and monoacetin (MA), were completely soluble in water due to their hydrophilic nature. Glycerol's multiple hydroxyl groups interact readily with water through hydrogen bonding, while acetic acid's dissociation into acetate ions and protons enhances its solubility. Monoacetin, structurally like glycerol and acetic acid, also exhibits high solubility.

Conversely, products from sunflower oil hydrolysis, such as diglycerides (DG), monoglycerides (MG), and free fatty acids (FFA), show limited solubility in water due to their hydrophobic characteristics (Fig. 2). The hydrophobic fatty acid chains in DG and MG tend to aggregate, reducing their solubility, while FFA's hydrophobic hydrocarbon tails dominate their interactions with water, resulting in sparing solubility. Depending on those phases the analysis and yields below depend on how the phases are analyzed [41]. Depending on those phases the analysis and yields below depend on how the phases are analyzed.

### 3.2. Hydrolysis of triacetin

The hydrolysis of triacetin (TA) in sub-supercritical water produced diacetin (DA), monoacetin (MA), glycerol (G), and acetic acid (HAc). The concentrations of TA, DA, MA, HAc, and G at various times are presented as a yield of the initial concentration in Fig. 3.

The TA concentration is dominant at low reaction times for all the temperatures, reflecting the primary component in the mixture. As reaction time rises, the TA concentration gradually decreases, giving way to higher concentrations of DA, MA, HAc, and G. This shift indicates the breakdown of TA into its constituent products, MA, DA, HAc, and G, during the hydrolysis process. Notably, the concentration of G and HAc rises at a larger reaction time, which is a sign of their accumulation as hydrolysis products. As expected, the yield of hydrolysis products is lower as the reaction temperature drops. It takes 11.2 s at 375C, 10.1 s at 385C, and 8.9 s at 400 °C to hydrolyze 98 % of TA. However, in 15 s at 300 °C, only 55 % of TA is hydrolyzed.

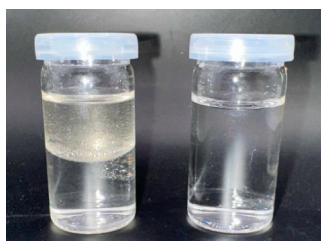The operation at 375 °C and 25 MPa seems to be a good balance



**Fig. 2.** Difference between sunflower oil (left) and triacetin (right) hydrolysis products.

between selectivity and energy efficiency. Specifically, at 11.2 s the selectivity is 42.5 % for DA, 46.0 % for MA, and 12.4 % for G. Comparing this with conditions at 385 °C and 25 MPa, the selectivity values shift to 27.2 % for DA, 45.4 % for MA, and 28.3 % for G. Increasing temperature 10 °C in supercritical water conditions (SCW) requires an additional energy input of 311 kJ/kg K. This increase in temperature, while beneficial for the reaction kinetics, comes with the added requirement for an extended reactor length due to the decrease in density at 385 °C. Balancing these factors is essential to optimize the trade-off between energy consumption and reactor design in pursuit of economic efficiency. Thus, 375 °C emerged as the most favorable option as it can be seen next from the conversion point of view.

### 3.2.1. Kinetic parameters of triacetin

The hydrolysis of esters is a reversible reaction and it has been studied by many authors. For example, the hydrolysis of ethyl acetate [31]; the subcritical water hydrolysis of sunflower seed oil [42], and the hydrolysis of soybean and canola oil [43,44]. Those studies were focused more on subcritical conditions and the reaction time to hydrolyze the triglyceride was long (up to 20 min).

The hydrolysis of triglycerides follows a two-main-step mechanism. Initially, thermal activation boosts molecular kinetic energy, facilitating the reaction. Acid-base catalysis, utilizing subcritical water containing hydronium and hydroxide ions, plays a crucial role. It protonates ester bonds in acidic conditions and deprotonates triglycerides in basic conditions, expediting nucleophilic attack and ester bond cleavage [33]. In supercritical water, the absence of additional catalysts is notable as the unique properties of water under high temperatures and pressures facilitate the hydrolysis reaction. The elevated conditions promote the rapid dissolution and activation of triglycerides, accelerating reaction rates. Mechanistically, this process involves a direct nucleophilic attack by water molecules on the ester bonds, resulting in the cleavage of glycerol and fatty acids.

Hydrolysis of triglycerides can be assumed a pseudo-homogenous, reversible first-order reaction that happens in the oil phase [28 33] as shown in Fig. 4. In the first step TA is hydrolyzed to DA, in the second step DA is hydrolyzed to MA and in the third step MA is hydrolyzed to G; in all steps, HAc is generated. The amount of HAc product is equivalent to the sum of three times the moles of G reacted, two times the moles of MA reacted, and one times the mole of DA. It is also equivalent to the total moles of water consumed. The formation of acetic acid acts as an acid catalyst, in this case, acetic acid (HAc) undergoes dissociation, resulting in the removal of a proton. This proton elimination leads to the protonation of the carbonyl oxygen of triglyceride (TG +), enabling the carbonyl carbon to become susceptible to nucleophilic attack by water molecules. This mechanism promotes the hydrolysis reaction of TA [33]. A similar series of reactions are carried out for DA and MA.

The concentration of TA inside the reactor is 2.72 %, the elevated concentration of water plays a pivotal role in several key aspects of the reaction. Firstly, it enables efficient solvation of the hydrophobic triglyceride molecules, enhancing their accessibility for reaction. Additionally, the high concentration promotes increased collision frequency between water molecules and reactants, facilitating faster hydrolysis reactions by readily attacking ester bonds. This concentration also aids in mass transfer, ensuring the swift transport of molecules to and from reaction sites[18,38].

The experimental and simulated data are presented in Fig. 5. Key constituents under examination include TA, DA, MA, and HAc. The hydrolysis yields are notably higher under supercritical conditions (375 °C, 385 °C, and 400 °C) compared to subcritical conditions (250 °C and 300 °C), attributed to water's heightened nonpolar characteristics, increased diffusivity, and decreased density under supercritical conditions, expediting hydrolytic reactions. The graph illustrates the formation of DA, peaking around 6 s at 375 °C and 25.0 MPa, followed by a decline with the formation of MA. DA and MA concentrations are notably higher in SCW, indicating faster reaction kinetics. Glycerol yield
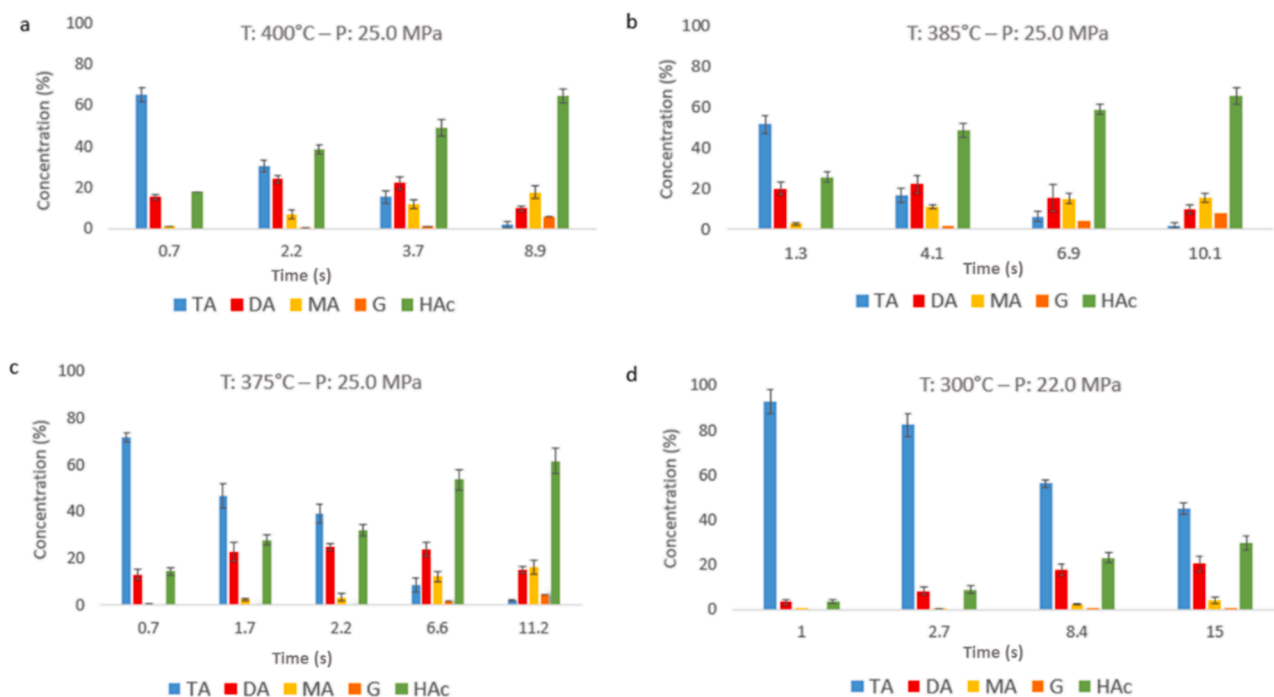
**Fig. 3.** Triacetin hydrolysis and product conversion at a: 400 °C – 25.0 MPa, b: 385 °C – 25.0 MPa, c: 375 °C – 25.0 MPa, d: 300 °C – 22.0 MPa over time.
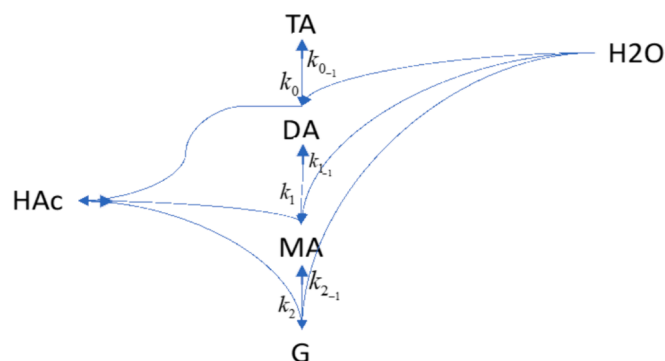


**Fig. 4.** Reaction Pathway for the hydrolysis of Triacetin.

after 11.2 s is low (approximately 4 %) and is not explicitly portrayed. Additional information on glycerol production is available for comprehensive insights. Acetic acid, with the highest yield, is consistently produced in every condition, increasing in quantity with longer reaction times.

The hydrolysis of triacetin in subCW and SCW is influenced by the properties of the reaction medium. Notably, higher temperatures lead to faster reaction rates due to increased molecular motion and collision frequency, which promotes the breaking of chemical bonds. Additionally, elevated temperatures enhance the solubility of reactants, making them more accessible for reaction. The dielectric constant of SCW, which relies on density and temperature, impacts solute–solvent interactions and the hydrolysis mechanism. The low dielectric constant of SCW promotes effective interactions with the hydrophobic segments of triglycerides, thereby influencing the efficiency of the hydrolysis process.

### 3.2.2. Activation energy for triacetin

The Arrhenius plot in Fig. 6 and the kinetic parameters listed in Table 2 reveal the temperature dependence of the hydrolysis reaction. The calculated activation energies and pre-exponential factors further validate the kinetic model, indicating a strong correlation between the observed data and the predicted reaction rates.

### 3.3. Hydrolysis of sunflower oil

Sunflower oil, with its higher molecular weight, increased non-polarity, and greater molecular complexity compared to triacetin, presents a higher challenge for hydrolysis. Therefore, the subsequent phase of this investigation provides comprehensive insights into the hydrolysis processes of this triglyceride within the framework of sub and supercritical water technology.

The hydrolysis of triglycerides in subcritical and SCW is analyzed through products yields at different time intervals (s) in Fig. 7. Initially, high concentrations of triglycerides (TG) are observed, gradually decreasing over time as triglycerides undergo hydrolysis, leading to increased concentrations of diglycerides (DG), monoglycerides (MG), free fatty acids (FFA), and G. Higher temperatures in supercritical conditions facilitate more efficient mass transfer, accelerating triglyceride hydrolysis compared to subcritical conditions, where the extent of hydrolysis is notably reduced due to lower TG solubility. At 29 s (Fig. 7-c), the composition of the hydrolysis products in SCW is as follows: 1.5 % TG, 16.3 % DG, 27.9 % monoglycerides MG, 48.9 % FFA, and 5.3 % G. This distribution elucidates the evolving molecular structure and relative abundance of constituents resulting from the hydrolysis of triglycerides under the influence of SCW at the specified time point. The observed proportions signify the progression of triglyceride breakdown, with a considerable proportion transformed into diglycerides, monoglycerides, and free fatty acids, indicating the hydrolysis process's effectiveness.

The selection of 375 °C and 25 MPa as the operating conditions is strategic and aimed at optimizing the hydrolysis process in terms of energy consumption, reaction efficiency, and selectivity. This condition demonstrates a high selectivity for DG and MG, essential for the targeted production of these compounds.

### 3.3.1. Kinetic parameters of sunflower oil

Fig. 8 shows the fittings of the experimental data with the simulated ones. The analysis of the data reveals a consistent trend in the transformation of TG to DG, MG, and FFA over time. The reactions were evaluated in a range of temperatures of 250 °C to 400 °C and pressures of 22.0 MPa and 25.0 MPa.
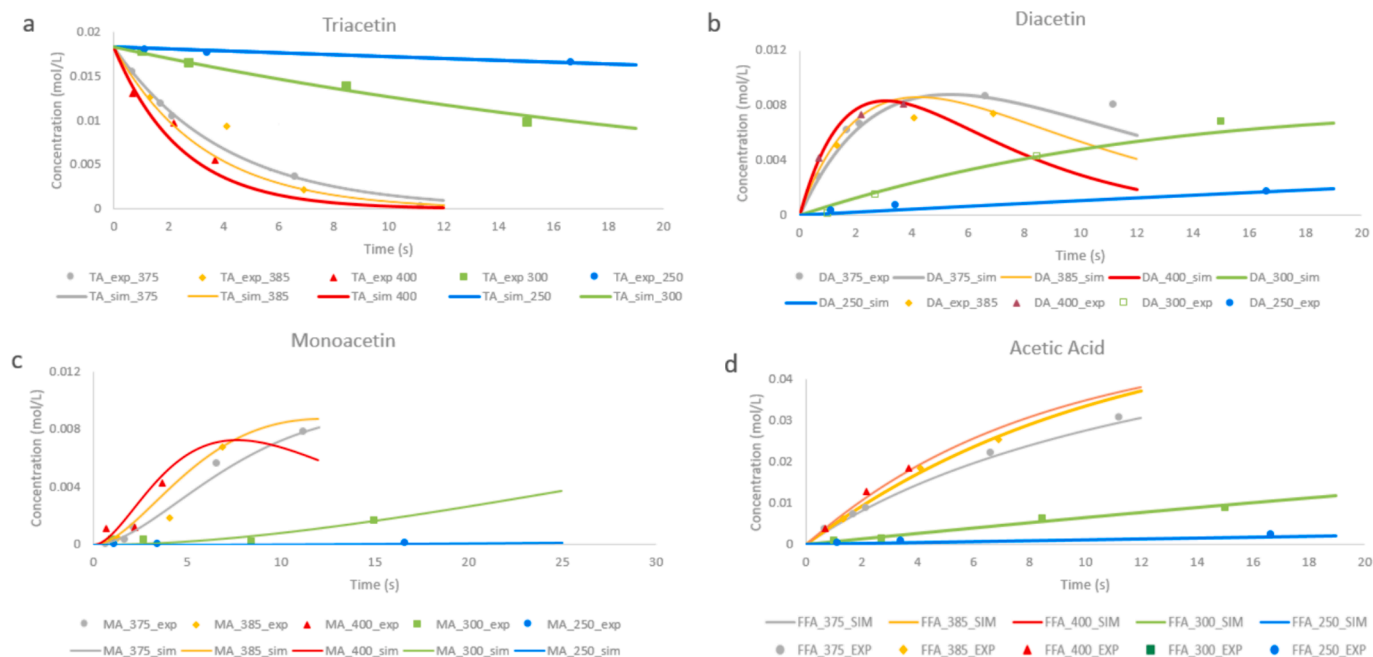
**Fig. 5.** Triacetin hydrolysis and formation of diacetin, monoacetin, and acetic acid at different temperature, pressure, and residence time.
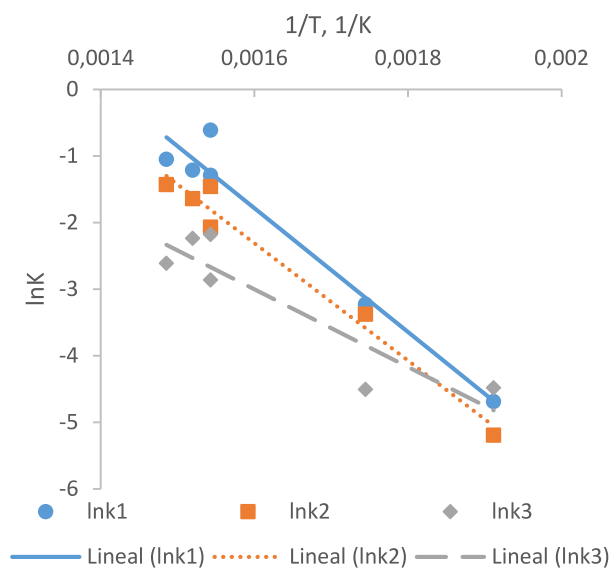


**Fig. 6.** Arrhenius plot for Triacetin hydrolysis.

**Table 2**
Kinetic parameters for Triacetin hydrolysis.

| Item | | k1 | k2 | k3 |
|---|---|---|---|---|
| Temperature (C) | Pressure (bar) | | | |
| 400 | 250 | 0.351 | 0.240 | 0.074 |
| 385 | 250 | 0.298 | 0.194 | 0.107 |
| 375 | 250 | 0.276 | 0.127 | 0.057 |
| 300 | 220 | 0.040 | 0.034 | 0.011 |
| 250 | 220 | 0.009 | 0.006 | 0.011 |
| Ea1 | | 77.3 | | |
| Ea2 | | | 73.3 | |
| Ea3 | | | | 48.9 |
| lnA | | 13.1 | 11.8 | 6.3 |
| R^2 | | 0.96 | 0.97 | 0.8 |

T: temperature (°C); k1, k2, and k3: rate constants ($s − 1[mol/mol$ of oil$] − 1$); Ea1, Ea2 and Ea3: energies of activation (kJ/mol); A: preexponential factor ($s − 1[mol/mol$ of oil$] − 1$).

than the ionic reaction in subcritical conditions[18].

### 3.3.2. Activation energy of sunflower oil

Fig. 9 and Table 3 show the Arrhenius plot for the kinetic constants of sunflower oil hydrolysis. The parameters suggest a direct correlation between temperature and the rate constants for the three reactions observed. Specifically, as the temperature rises, there is a noticeable increase in the rate constants for all three reactions. Moreover, the transition from subcritical to supercritical conditions markedly accelerates reaction rates, showing significantly slower reactions in the subcritical state. The reaction of glycerol production exhibits the highest activation energy at 152.2 kJ/mol, followed by the formation of di-glycerides from triglycerides, requiring an activation energy of 101.3 kJ/mol. Comparatively, the formation of monoglycerides from di-glycerides exhibits the lowest energy barrier for activation at 50.9 kJ/mol, which shows its relatively faster reaction.

These observations elucidate the temperature sensitivity of the reactions and the substantial impact of transitioning from subcritical to supercritical conditions on the reaction rates. The trend in activation energies reflects that the formation of glycerol requires the highest energy input, while the production of monoglycerides from diglycerides necessitates the least energy for initiation. The kinetic constant also
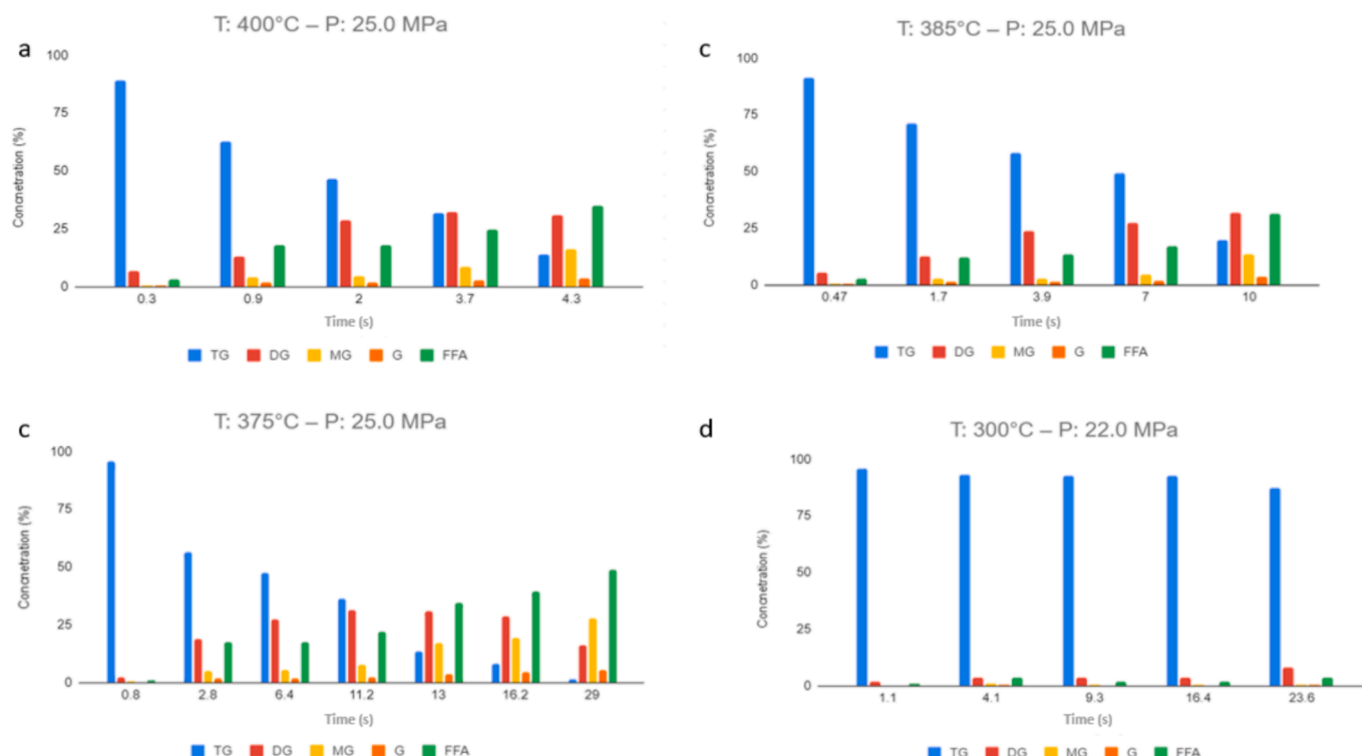
As expected, the TG concentrations decrease with time for all conditions. Higher temperatures lead to faster hydrolysis rates, resulting in lower TG concentrations at each time point. DG concentrations increase with time until a peak concentration. After the maximum, the concentration decreases as the DG is hydrolyzed. Higher temperatures result in higher DG concentrations, indicating faster conversion. MG concentrations also increase with time, demonstrating the further breakdown of DG into MG during hydrolysis. Higher temperatures lead to higher MG concentrations, indicating more rapid MG formation after a maximum MG leads to the formation of glycerol. FFA concentrations increase with time, indicating the complete hydrolysis of TG, DG, and MG into fatty acids. Higher temperatures result in higher FFA concentrations, suggesting faster conversion of glycerides to fatty acids and glycerol. The impact of autocatalysis on reaction times is negligible, with a low effect observed under both subcritical and supercritical conditions. This is because in supercritical conditions the radical reaction is more favorable

**Fig. 7.** Sunflower oil hydrolysis and products yields at a: 400 °C – 25.0 MPa, b: 385 °C – 25.0 MPa, c: 375 °C – 25.0 MPa, d: 300 °C – 22.0 MPa over time.
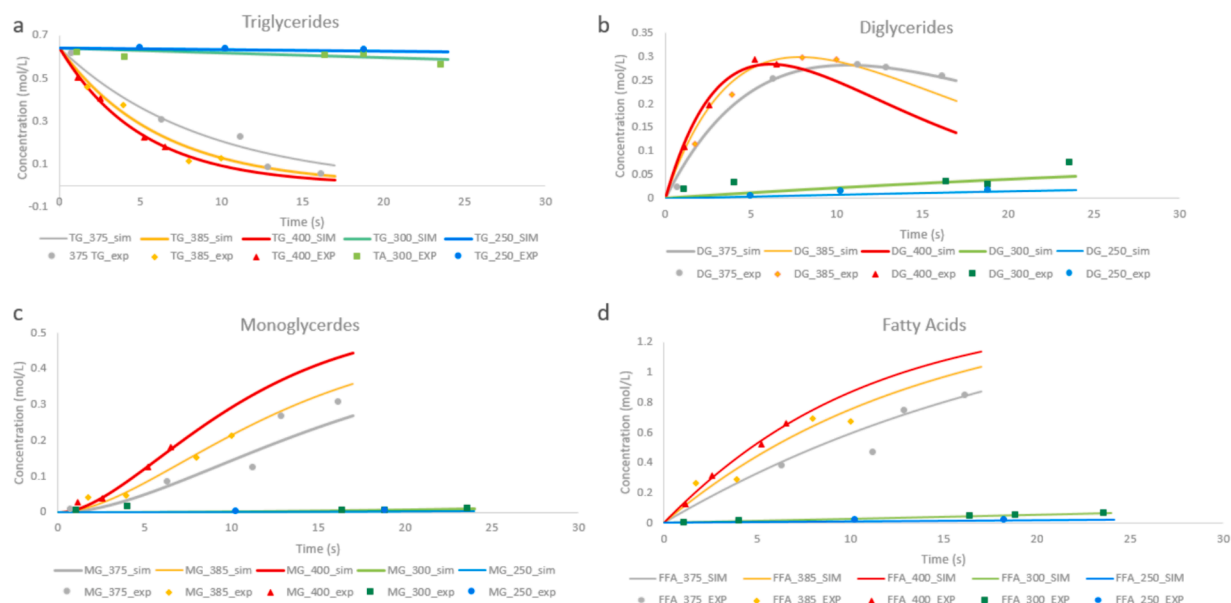


**Fig. 8.** Sunflower oil hydrolysis and formation of diglycerides, monoglycerides, and fatty acids at different temperatures, pressures, and residence time.

affects the selectivity. Increasing the temperature means that the conversion of the reagent is faster. Fast reactions are more difficult to control and in this case, the selectivity of the DG and MG would be more challenging.

The kinetics constants shown in Fig. 9 can be analyzed to understand the higher yield of mono and glycerides found at 375C. All the kinetic constants are increased when the reaction temperature is increased. However, the rates of triglycerides and diglycerides hydrolysis are increased less than the hydrolysis rate of monoglycerides. Then, the rate difference between monoglyceride production and hydrolysis is smaller at high temperatures than at low temperatures. This can be seen when

comparing the grey line to the blue/orange lines in Fig. 9. As a consequence of this, lower reaction temperatures will promote the production of higher yields of mono and diglycerides.

### 3.3.3. Selectivity comparison

Fig. 10 shows the production of DG and MG together as a function of reaction time at different temperatures. The graph reveals that maximum yields of DG and MG are attained at 375 °C for both triacetin and sunflower oil. Notably, the data indicates a decrease in selectivity for mono- and diglycerides beyond this temperature threshold, suggesting a reduction in their production efficiency with increasing
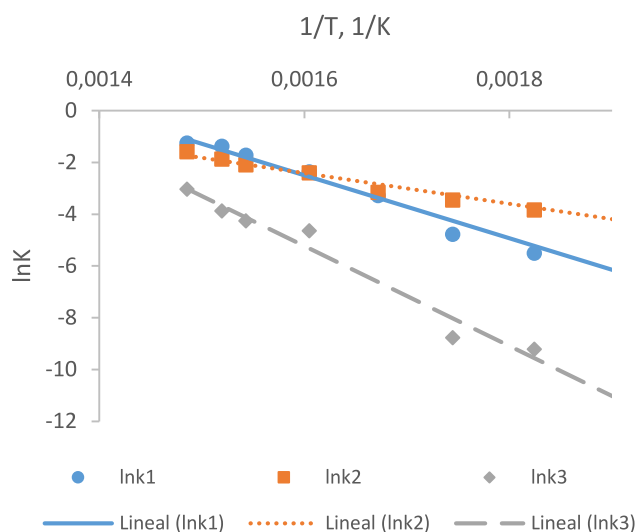
## 1/T, 1/K



**Fig. 9.** Arrhenius plot of Sunflower oil hydrolysis.

**Table 3**
Kinetic Parameters of Sunflower Oil Hydrolysis.

| Item | | k1 | k2 | k3 |
|---|---|---|---|---|
| Temperature (C) | Pressure (bar) | | | |
| 400 | 250 | 0.289 | 0.207 | 0.048 |
| 385 | 250 | 0.256 | 0.154 | 0.021 |
| 375 | 250 | 0.181 | 0.125 | 0.014 |
| 350 | 220 | 0.095 | 0.091 | 0.009 |
| 325 | 220 | 0.034 | 0.043 | 0.012 |
| 300 | 220 | 0.008 | 0.032 | 0.0002 |
| 275 | 220 | 0.004 | 0.018 | 0.0001 |
| 250 | 220 | 0.003 | 0.019 | 0.000 |
| Ea1 | | 101.3 | | |
| Ea2 | | | 50.9 | |
| Ea3 | | | | 152.2 |
| lnA | | 16.9 | 7.4 | 24.3 |
| R^2 | | 0.97 | 0.95 | 0.86 |

T: temperature ($\circ$C); k1, k2, and k3: rate constants ($s - 1[\text{mol/mol of oil}] - 1$); Ea1, Ea2 and Ea3: energies of activation (kJ/mol); A: preexponential factor ($s - 1[\text{mol/mol of oil}] - 1$).

temperature. The data illustrates that the highest production of mono- and diglycerides at 375 $\circ$C is found at 6.3 s. That yield is higher than the ones at 385 $\circ$C (5.1 s) and 400 $\circ$C (4.3 s). This observation suggests that 375 $\circ$C is the optimal temperature for maximizing the production of mono- and diglycerides from sunflower oil. Furthermore, the graph

elucidates the time required to achieve the highest productivity of mono- and diglycerides at distinct temperatures. In the case of sunflower oil, a visual observation reveals that the maximum yield occurs at 26 s at 375 $\circ$C, 16.2 s at 385 $\circ$C, and 11.4 s at 400 $\circ$C.

### 3.3.4. Comparison between triacetin and sunflower oil kinetic parameters

A comparison between the kinetic constant for triacetin and sunflower oil hydrolysis at different temperatures is presented in Fig. 11. Triacetin exhibits higher rate constants (k) and lower activation energies (Ea) compared to sunflower oil. This is attributed to the differences in chemical structure and reactivity of the two substances. Triacetin (glycerol triacetate) has a simpler chemical structure than sunflower oil, a complex mixture of triglycerides. It has three acetyl groups attached to the glycerol backbone. The simpler structure of triacetin allows for easier accessibility of hydrolyzing agents to the acetyl groups, leading to a faster reaction rate.

The acetyl groups in triacetin are more reactive compared to the fatty acid chains in sunflower oil. Acetyl groups are more susceptible to hydrolysis due to the presence of easily hydrolyzable ester bonds. In sunflower oil, the fatty acid chains are longer and have more saturated or unsaturated bonds, making them less susceptible to hydrolysis. Triacetin's smaller molecular size and simpler structure enable hydrolyzing agents to reach and break the ester bonds more easily, resulting in a higher reaction rate. On the other hand, the larger and more complex molecular structure of sunflower oil makes it less accessible for hydrolysis, leading to lower reaction rates. The lower activation energy (Ea) for triacetin indicates that less energy is required to initiate the hydrolysis reaction. The simpler structure and higher reactivity of triacetin's acetyl groups contribute to this lower activation energy. In contrast, the more complex and less reactive structure of sunflower oil's fatty acid chains necessitates a higher activation energy to initiate hydrolysis. Overall, sunflower oil takes 3- 4X more reaction time to reach peak yields of mono and diglycerides.

### 4. Conclusions

Triacetin was used as a model compound and later transitioned to the more complex sunflower oil. Notably, 98 % of triacetin conversion was achieved within 11.2 s at 375C and 25 MPa. A similar degree of hydrolysis for sunflower oil was attained at 29 s. When comparing same reaction time and temperature, the conversion of triacetin was 92 % at 11.2 s, while the conversion of sunflower oil was 82 % at 11.2 s. A kinetic model comprehensively characterized the reaction kinetics and monitored component concentrations at various reaction times. From the kinetic model, it was noted that the activation energy values for the hydrolysis reactions differ between triacetin and sunflower oil. Specifically, for triacetin, the activation energy values were $Ea_1 = 77.3$, $Ea_2 =$
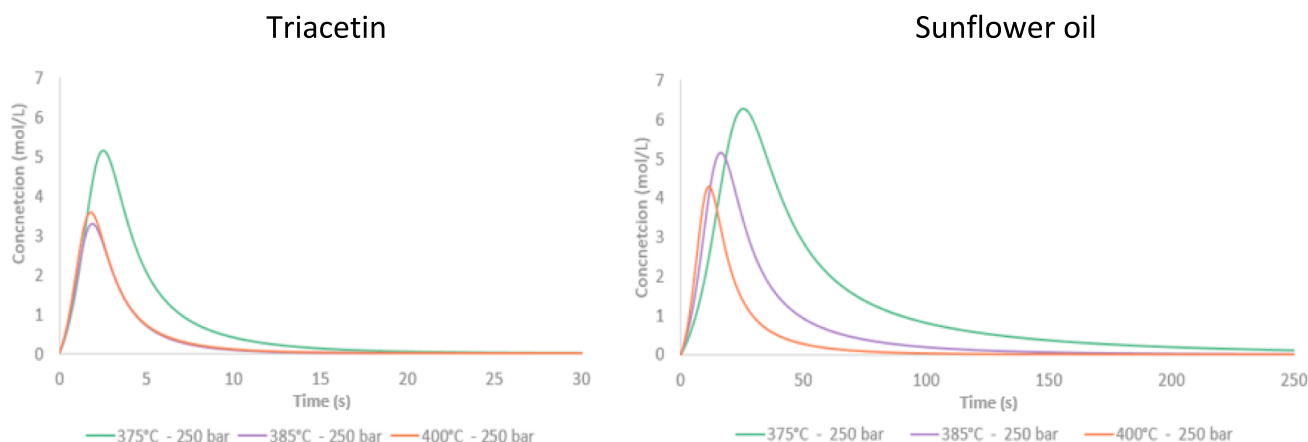
## Triacetin

## Sunflower oil
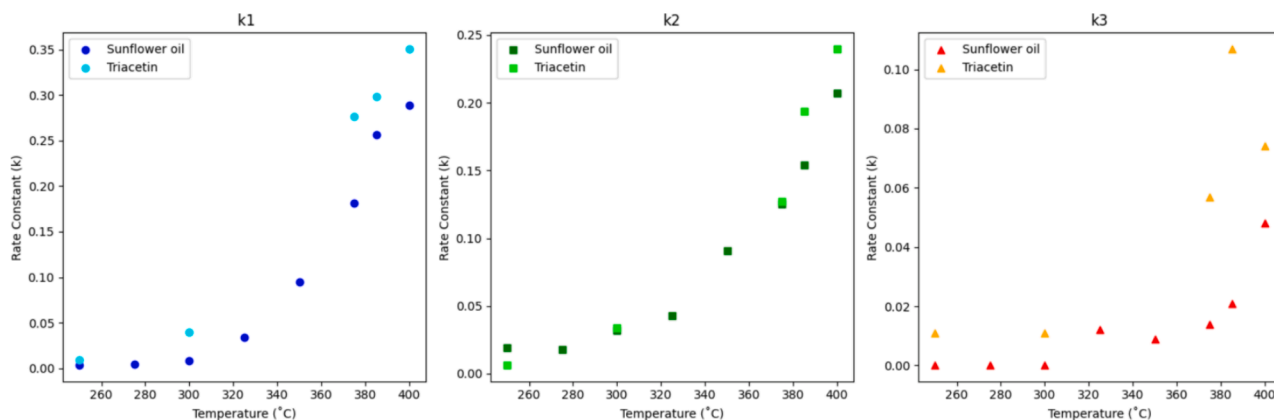


**Fig. 10.** Impact of Temperature on Selectivity.

**Fig. 11.** Comparison of kinetic parameters between triacetin and sunflower oil.

73.3, and Ea$_3$ = 48.9, while for sunflower oil, the corresponding values were Ea$_1$ = 101.3, Ea$_2$ = 50.9, and Ea$_3$ = 152.2. This discrepancy is being ascribed to various factors, encompassing molecular mass, structural intricacy, and solubility of the molecules involved. This case serves as an exemplification, underscoring the necessity for meticulous consideration when dealing with ester-based compounds of heightened complexity, such as polyesters. Due to their elevated molecular intricacy, reduced solubility, slower rates of mass transfer, and potentially greater heterogeneity in fatty acid constituents, managing these intricate compounds poses increased challenges, demanding prolonged reaction residence times.

Supercritical water technology offers notable advantages in achieving precise reaction selectivity, allowing fine-tuned control over reaction times in seconds. For example, tailoring the process to prioritize monoglyceride production over fatty acids becomes achievable through meticulous time adjustments. In the kinetic model, it is observed that after 44 s at 375 °C and 25 MPa, the concentration of monoglycerides begins to decline, leading to the production of glycerol and fatty acids. Increasing the reaction time contributes to a decrease in monoglyceride levels, and elevating the temperature enhances kinetic constants, thereby accelerating the reaction rate. For instance, the product concentrations are higher at 385 °C with the same reaction time. The temperature rise also reduces density and viscosity, facilitating better penetration of water into oil and expediting the hydrolysis reaction. Additionally, increased temperature enhances the solubility of oil in water.

Transitioning from subcritical to supercritical conditions induces significant changes in product concentrations. Optimal conditions in supercritical water are chosen at 375 °C and 25 MPa, considering both energetic. However, it is crucial to note that raising the temperature by 10 °C in supercritical water demands an additional energy input of 311 kJ/kg K. Although this temperature increase benefits reaction kinetics, it necessitates an extended reactor length due to the lower density of the system at 385 °C. Another favorable aspect of supercritical conditions is the higher selectivity and improved pressure control. SCW hydrolysis of triglycerides proves to be swift and highly efficient, positioning it as the fastest known method for triglyceride hydrolysis.

**CRediT authorship contribution statement**

**Enkeledo Menalla:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Juan García Serna:** . **Danilo Cantero:** Writing – review & editing, Validation, Software, Formal analysis, Conceptualization. **María José Cocero:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

Data will be made available on request.

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