# Continuous Flow Hydrolysis of Sunflower Oil Using Sub-critical Water

R. Alenezi, M. N. Baig, R.C.D Santos, G.A. Leeke*
Department of Chemical Engineering, The University of Birmingham,
Edgbaston, Birmingham, B15 2TT, UK,
*G.A.Leeke@bham.ac.uk, fax: +441214145324

## ABSTRACT

The use of sub-critical water has recently been proven to be a successful medium for conducting hydrolysis reactions without employing acid or alkali catalysts. This work presents the usage of sub-critical water as both solvent and reactant for the continuous flow hydrolysis of sunflower oil (triglyceride) in a tubular reactor. The hydrolysis products of sunflower oil are fatty acids and glycerol. Fatty acids are an important intermediate product for many industrial applications. Experiments were undertaken between pressures of 100 to 200 bar and temperatures of 270 to 350 ºC. The water to oil ratio was 50:50 v/v. Fatty acid was found to act as an acid catalyst that allowed a simple process and high yield. The rate of the hydrolysis was enhanced by increasing temperature and residence time. The highest yield up to 90% was obtained at the conditions of 8 minutes reaction time, 50:50 v/v water oil ratio, 200 bar and 350 ºC. The results show promise for integration of a continuous flow hydrolysis and an esterification process into a one step continuous procedure for biodiesel production.

Keywords: subcritical water, hydrolysis, fatty acids, sunflower oil.

### INTRODUCTION

The development of environmentally friendly processes has become highly desired recently for reasons such as pollution prevention, public acceptance and hazard elimination. Many researchers in several areas have offered to develop these green processes, for examples; the usage of biomass for energy sources, and the usage of supercritical fluids to prevent problems with organic solvents. Avoiding the usage of organic solvents is a major factor in any process, simply because these solvents need to be separated, recycled, incinerated, or submitted to other utility process that does not discharge harmful materials to the environment.

Water in the sub and supercritical states provides therefore unique properties over its ambient condition properties [1-3]. Many studies have been undertaken to use solvents in water near its critical condition (374 ºC, 221 bar) to eliminate organic solvent in synthesis [4-7]. The major two advantages of sub-critical water are its a relatively large ion products and low relative permittivity. Relative permittivity of sub-critical water is comparable with that of acetone or methanol at ambient conditions and can be adjusted from a room temperature value of 80 to 5 at its critical point.

Hydrolysis reactions are important in the processing of oil and fats for chemical industry [3]. Hydrolysis reaction of oil can be defined as an operation in which sub-critical water reacts with oil (triglyceride) to form fatty acids and glycerol. Fatty acids and glycerine are important raw materials as intermediates for biodiesel and for soap production, synthetic detergents, greases, and cosmetics [8]. In the sub-critical state, water can act as both solvent and reagent for the hydrolysis of triglyceride [5, 7]. Some researchers have found it advantageous to use pressures greater than 200 bar and temperatures over 250 ºC as it avoids using either acidic or alkaline catalysts [5, 9, 10].

The hydrolysis reaction as shown in Figure 1 has been proposed by many researchers as three stepwise reactions: (1) triglyceride (TG) is hydrolyzed to diglycerides (DG), (2) DG is hydrolyzed to monoglycerides (MG), (3) MG is hydrolyzed to glycerol, and in each step there is a production of a fatty acid (FA). This reaction is a homogenous first order reversible reaction in the oily phase[4]. It has been shown that FA can act as acid catalyst in the hydrolysis reaction of oil in sub-critical water and can achieve up to 90wt.% without employing a catalyst [8]. This non-catalytic reaction will prevent the removal of catalyst from the final product which is technically difficult, and bring extra cost to the final product [11].

$$\underset{\text{triglyceride}}{C_3H_8\,(OOCR)_3} + \underset{\text{water}}{H_2O} \longleftrightarrow \underset{\text{diglyceride}}{C_3H_8\,(OH).(OOCR)_2} + \underset{\text{fatty acid}}{RCOOH}$$

$$\underset{\text{diglyceride}}{C_3H_8\,(OH).(OOCR)_2} + \underset{\text{water}}{H_2O} \longleftrightarrow \underset{\text{monoglycride}}{C_3H_8\,(OH)_2.\,(OOCR)} + \underset{\text{fatty acid}}{RCOOH}$$

$$\underset{\text{monoglycride}}{C_3H_8\,(OH)_2.(OOCR)} + \underset{\text{water}}{H_2O} \longleftrightarrow \underset{\text{glycerol}}{C_3H_5(OH)_3} + \underset{\text{fatty acid}}{RCOOH}$$

**Figure. 1**. Hydrolysis reaction of vegetable oil.

In this paper a non-catalytic continuous flow hydrolysis reaction of sunflower oil was performed in sub-critical water at (100 to 200 bar, 270 to 350 ºC). The continuous flow process offers the advantage of large-scale production. For a low value product, the extra cost incurred by working at supercritical conditions would not be economically viable and would be detrimental to product integrity. The conditions that affect the yield of FA and rate of reaction were investigated.

## MATERIALS AND METHODS

Sunflower oil was purchased from a leading UK supermarket chain. Since sunflower oil consists of at least 96.5% triglycerides; 2.5% diglycerides; 0.8% sterol ester and only 0.3 to 0.5% fatty acids, then sunflower oil can be assumed to be triglycerides[12]. Distilled and deionized water is used in order to prevent scaling on the walls of the tube reactor and ancillary piping at the reaction conditions.

Figure 2 shows the laboratory–scale setup of the equipment used for hydrolysis of sunflower oil under continuous conditions. In this system, TG and water were separately fed from the columns into the tubular reactor though a mixer device by two HPLC pumps. The reactor was made from stainless steal tubing which had a dimension of 60 ml in volume and 4 m in length and was housed in an electrical furnace. The pressure in the reactor was controlled by a back pressure regulator valve. In this way, the temperature and the pressure inside the reactor coil were continuously maintained at the desired operational conditions. The temperature of the products leaving the reactor was lowered in a cooling unit to ambient temperature. The reaction time was calculated by dividing the volume of the reactor by volumetric flow rate of the sunflower oil and distillate water at desired reaction conditions in the following equation (1) [8]:

$$t = \frac{V}{F_w \frac{\rho_w}{\rho'_w} + F_o \frac{\rho_o}{\rho'_o}} \quad (1)$$

Where V is the volume of the reactor. $F_w$, is the setting flow rate of water (ml/min) and the $\rho_w$, $\rho'_w$ are the densities (g/ml) of the water at the normal ambient condition and reaction condition respectively. $F_o$ is the flow rate of oil (ml/min) and the $\rho_o$ and $\rho'_o$ are the densities (g/ml) of the sunflower oil at the normal ambient condition and reaction condition respectively, and assumed to be equal at the reaction condition. At the end of the system samples were collected at regular time intervals. The product from hydrolysis was gravity separated into two portions, the upper portion was mainly FA, unreacted TG and intermediate compounds (DG and MG), and the lower portion is glycerol. The hydrolysis reaction conditions ranged between a temperature of 250 to 350 ºC and pressures of 100 to 200 bar.

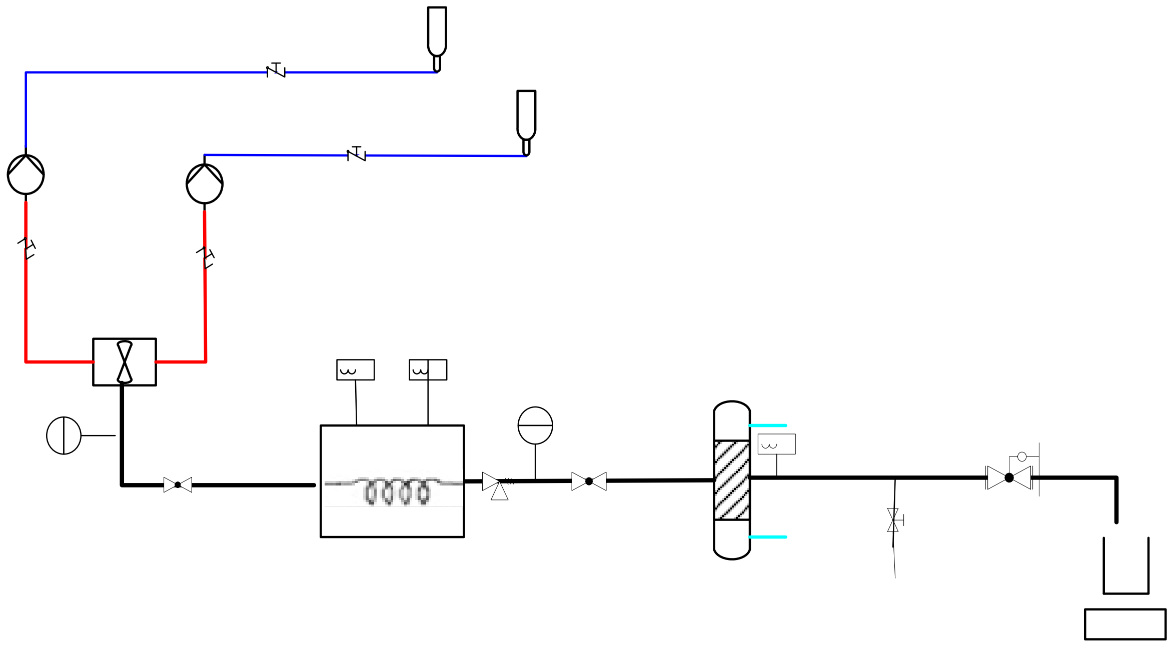

**Figure 2**. Continuous flow hydrolysis rig.

The concentration of FA was analyzed using High Performance Liquid Chromatography (HPLC); Agilent 1100 series with Chemstation Chromatography Software. The HPLC was fitted with an Agilent 1200 Refractive Index Detector (RID), and Eclipse Plus C8 column at a constant temperature of 40 ºC. Methanol HPLC-grade eluent was used at a flow rate of 1

Feed Column

ml/min. Although sunflower oil consists of various fatty acids, the major one is linoleic acid constituting about 72% of all other fatty acids [13]. A calibration curve was constructed for linoleic acid with correlation of 0.999 for quantitative analysis. Linoleic acid [60-33-3] was purchased from Sigma-Aldrich, having a given purity of 99.5 % and was used as received.

## RESULTS

The hydrolysis experiment of sunflower oil in sub-critical water was carried out in a tubular reactor. If plug flow conditions are assumed, the temperature and the pressure inside the reactor coil are constant for different operational conditions. Temperature, pressure and residence time (flow rate) were all studied to find the best operation conditions for optimal FA yield.

*Effect of reaction temperature on the yield of FA.*

Hydrolysis reactions were carried out at various temperatures ranging from 270 to 350 ºC with water/oil ratio 50:50 v/v. Figure 3 demonstrates the effect of reaction temperature on the yield of FA. The yield of FA at 270 °C in the first 10 min was low, however it increased with reaction time, it can be clearly seen that the maximum yield obtained at 270 ºC was about 71%. The rate of FA becomes higher when the temperature increased Figure 3. The highest yield up to 90% was obtained at the conditions of only 8 minutes reaction time, 200 bar and 350 ºC. The same yield was obtained in 12 minutes at 330 ºC and 24 minutes at 300 ºC. As water and oil are insoluble at low temperature and pressure, the reaction in these conditions is extremely slow. Increasing the temperature increases the oil solubility in water and the speed of the reaction accelerates quickly [5].

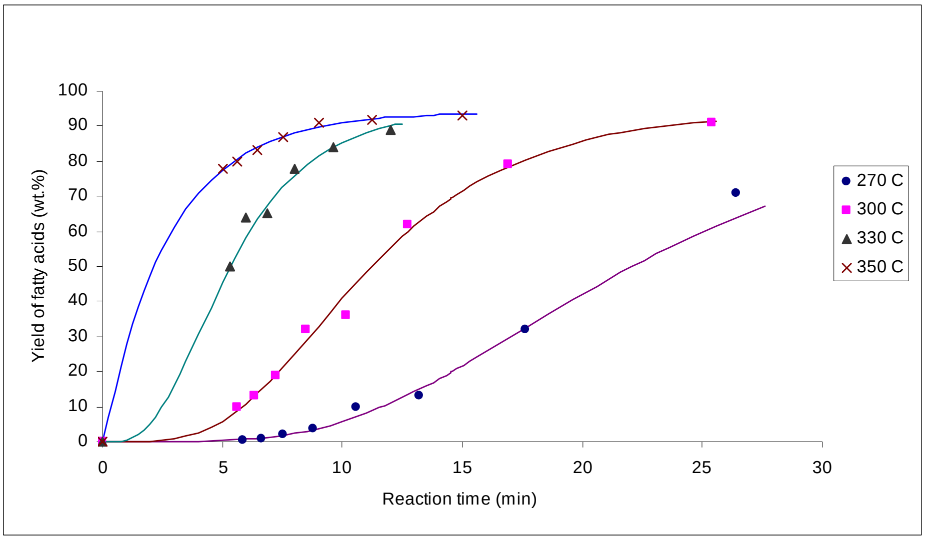


**Figure 3**. Effect of temperature on the yield of fatty acids from the continuous hydrolysis of sunflower oil with water to oil ratio 50:50 at 200 bar.

*Effect of reaction pressure on the yield of FA.*

The effect of reaction pressure on the yield of FA at a water oil ratio of 50:50 v/v and 300 ºC is shown in Figure 4. The yield of FA increased slightly when the pressure is doubled from 100 to 200 bar. At a reaction time of approximately 25 minutes a conversion of 90% is achieved at 200 bar compared to 86% conversion 100 bar. This result indicates that the pressure is less important in the degree of hydrolysis in contrast to the effect of reaction temperature.

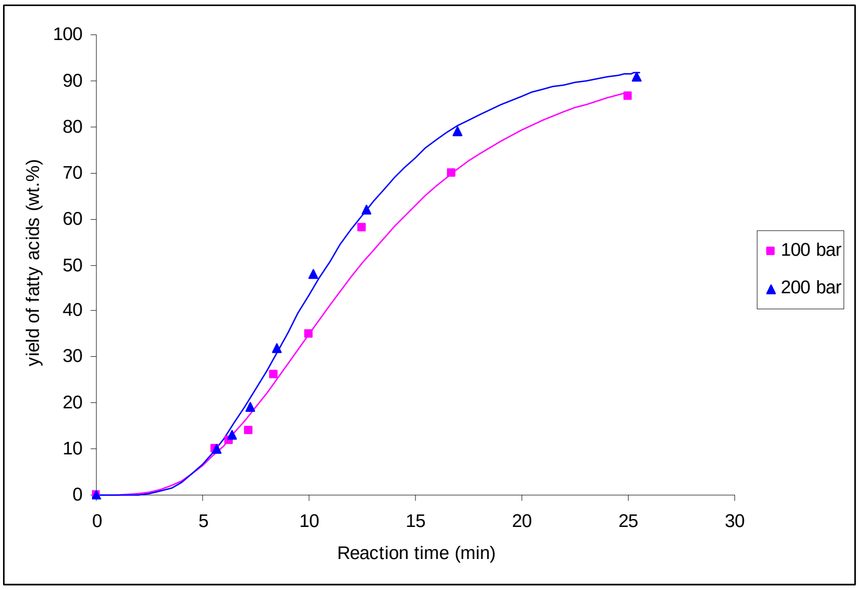


**Figure 4**. Effect of pressure on the yield of free fatty acids from the continuous hydrolysis of sunflower oil with water to oil ratio 50:50 at 300 °C.

*Change of FA Yield with water density.*

The relationship between water density and the degree of hydrolysis is shown in Figure 5. The density of water between 0.73 to 0.78 g/ml results in a lower FA conversion of about 35%. A large change in the conversion occurred when the density of water is less than 0.73 g/ml. The density of water therefore has opposite behavior on the degree of hydrolysis; because of the effect of the reaction temperature.

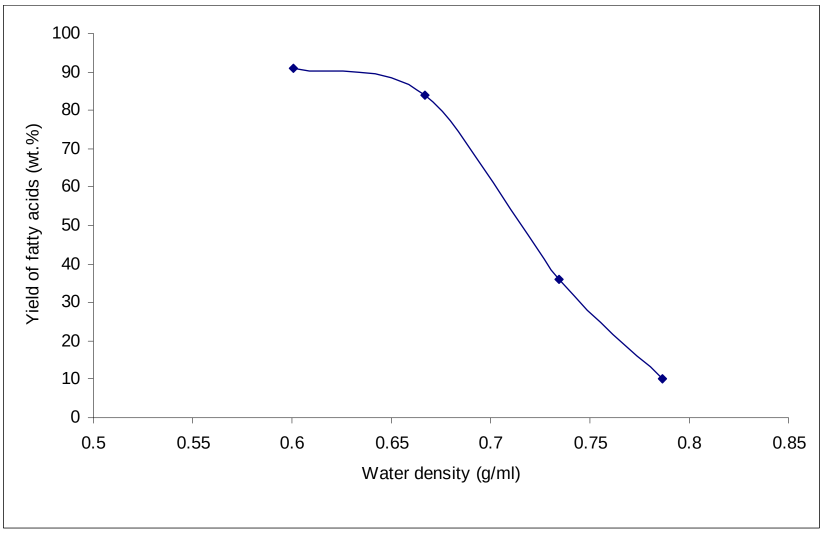


**Figure 5**. Effect of water density on the yield of fatty acids from the continuous hydrolysis of sunflower oil with water to oil ratio 50:50.

## CONCLUSION

The use of subcritical water in continuous flow hydrolysis reaction has been proven to be an effective method to produce a high concentration of fatty acids from sunflower oil. It has been found that the rate of hydrolysis is strongly affected by temperature and the reaction time. In order to achieve quantitative hydrolysis there is a need to extend the reaction time but care should be taken to avoid the thermal degradation of the products. The reaction pressure in the oil hydrolysis has been found a minor effect on the yield of fatty acids. Hydrolysis reaction with high yield up to 90% can be achieved without any catalysts; this is because fatty acid acts as an acid catalyst in a hydrolysis reaction of oil/fat in subcritical water.

.

## REFERENCES:


[1] Khuwijitjaru, P., Fujii, T., Adachi, S., Kimura, Y., Ryuichi Matsuno, R., Chemical Engineering Journal, Vol. 99, **2004**, P.1-4

[2] Clifford, T., Fundamentals of Supercritical Fluids, **1999**, New Yourk: Oxford University Press. 22-23.

[3] Russell L. Holliday, J.W.K.,vol. 36, **1997**, p. 932-35.

[4] Ackelsberg, O.J., Journal of the American Oil Chemists Society, Vol. 35 **1958,** p. 635.

[5] Pinto, J.S.S. and F.M. Lancas, Journal of the Brazilian Chemical Society, Vol. 17 **2006**, p. 85-89.

[6] Lascaray, L., The Journal of the American Oil Chemists Society, Vol. 29, **1952**, p. 362.

[7] Partil, T.A., Industrial engineering chemistry research, Vol. 27, **1988**, p. 727-735.

[8] Lawrence, E.A., The Journal of the American Oil Chemists Society, Vol. 31, **1954**,p. 542.

[9] Minami, E. and S. Saka, Fuel, Vol. 85, **2006**, p. 2479-2483.

[10] Kusdiana, D. and S. Saka, Applied Biochemistry and Biotechnology, Vol. 113 **2004**, p. 781-791.

[11] Demirbas, A., Energy Conversion and Management, Vol. 44, **2003**,p. 2093-2109.

[12] Weatherley, L.R. and D. Rooney, Chemical Engineering Journal,Vol. 135, **2008**, P. 25-32

[13] Yuan, W., A.C. Hansen, and Q. Zhang, Fuel, Vol. 84, **2005**, p. 943-950.