

GLYCEROL AND METHYLESTERS DECOMPOSITION IN THE SUPERCRITICAL PRODUCTION OF BIODIESEL: POTENTIAL ALTERNATIVE TO IMPROVE FUEL CHARACTERISTICS AND YIELD

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In this work, the supercritical transesterification of fat with methanol was studied at temperatures 350 to 400 °C, pressures to 300 bars and methanol to fat molar ratios 3:1 to 12:1 in a continuous unit. The identified products in the biodiesel phase included not only the long chain methylesters but also small chain methylesters originated in the decomposition reactions of long chain methylesters, as well as linear alkanes and alkenes. In the aqueous phase several glycerol decomposition products were identified. Glycerol methanolysis and dehydration reactions originated several byproducts such as glycerol ethers and polyglycerols. Some of these products have been used as fuel or fuel additives and therefore could increase the yield of the biodiesel and improve certain properties of the fuel.

Keywords: supercritical transesterification, glycerol, methylesters, decomposition.

INTRODUCTION

Biofuels economy development has been strongly encouraged in Colombia due to an expected decrease in oil sources in the near future. In this aspect, inherent advantages of biofuels, not only those associated with the sustainability and environmental friendliness but also with the possibility of reducing the dependence on imported fuels, have promoted the research of different production alternatives. Currently biodiesel is produced by the conventional base catalyzed method at an industrial level. However, it is well known that production costs are prohibitive due mainly to the price of refined vegetable oils, and that the process is not economically feasible without government subsidies [1]. In order to reduce the production costs and make biodiesel cost attractive in comparison to oil derived fuels, processes must make use of cheaper feedstocks such as waste oils and animal fats [2,3]. Nevertheless, conventional biodiesel production processes cannot make use of such feedstocks in an efficient way due to the high content of free fatty acids and water, which deactivate the catalysts and make the separation from byproduct glycerol difficult [4].

Initially pioneered by Japanese researchers, the supercritical transesterification process with methanol has successfully addressed the limitations the conventional acid and base catalyzed process has with low quality raw materials, due to the elimination of the necessity

of a catalyst [5]. This process is usually carried out at temperatures and pressures higher than 300 °C and 100 bar (98.7 atm) respectively and very high methanol to triglycerides molar ratios, usually 42:1. Different economical analysis performed to the supercritical process in comparison to conventional processes have shown promising results [1].

In spite of the widely reported advantages of the supercritical process, not only the possibility of using low quality raw materials but also the short reaction times [6], most of the experimental studies have been carried out with refined vegetable oils. In addition, the high methanol to triglycerides molar ratios required for the transesterification make the process economically unfeasible due to the costs involved in preheating and pressurization of methanol in excess at supercritical conditions, as well as the recycling of methanol. The use of excess methanol in the supercritical process has been attributed to the necessity of driving the chemical equilibrium to the products side [2] and to a reduction of the critical temperature of the mixture that allows carrying out the reaction in a homogeneous phase [7].

Most supercritical transesterification studies have been carried out in the temperature range 300 to 350 °C, due to the possibility of biodiesel decomposition, which has been reported at temperatures higher than 350 °C. Although not much information is available about this decomposition, it is generally accepted that it conduces to biodiesel degradation [8].

Recent research works have shown that the supercritical process for producing biodiesel can be carried out at moderate excess methanol and reaction temperatures higher than 350 °C, promoting at the same time the byproduct glycerol decomposition [1,9,10]. Due to the increased biodiesel production worldwide, glycerol recovery and sell as a valuable product has become unattractive, as prices keep to plummet, and therefore glycerol is practically a residues issue. In this sense, the simultaneous decomposition of glycerol in the supercritical transesterification process is very promising from a process engineering standpoint. However, not much information is available on the decomposition products of glycerol at supercritical conditions.

In this work, the biodiesel and glycerol decomposition products obtained during the chicken fat supercritical transesterification with moderate excess of methanol and temperatures higher than 350 °C are discussed. Experimental results suggest it is feasible to produce biodiesel at these conditions and that the decomposition products from methylesters and glycerol have the potential to improve certain fuel characteristics of biodiesel obtained through conventional methods such as a high viscosity and poor cold flow.

EXPERIMENTAL SECTION

Chicken fat supercritical transesterification runs were carried out in a continuous unit setup comprised of high pressure pumps, electrical resistances and isothermal oven and a depressurization valves. Additional details on equipment capacity and reactor and preheaters length is available elsewhere [11]. Experimental runs were carried out in the temperature range 350 to 450 °C, pressures in the range 100 to 300 bars (98.7 to 296 atm), methanol to fat molar ratios from 3:1 to 12:1 and residence times from 3 to 10 minutes. The selection of operation conditions was based on experimental results by Anitescu et al [1], who showed it was possible to obtain high triglycerides conversions to biodiesel with stoichiometric molar

ratios and temperatures of 400 °C. The use of low molar ratios was also intended to produce lower processing costs by the supercritical method.

In a typical experimental run the reactor is preheated to the reaction temperature and methanol is pumped to purge the system. Methanol and chicken fat flow rates are set according to the residence time for that run. Once steady state is attained inside the reactor samples are collected in a vessel submerged in an ice bath. Samples are directly analyzed without pretreatment. Methyl esters were measured in a HP 5890 gas chromatograph equipped with a HP-1MS column 30 m × 0.25 mm × 0.25 μm and a mass spectrometer detector. Temperature program was started at 60 °C and kept for 2 minutes for a subsequent 4 °C per minute ramp to 270 °C. Sample injection was carried out at 250 °C. Free and bound glycerol were measured in a HP 5890 Series II chromatograph with a flame ionization detector and a Restek Rtx-Biodiesel TG column according to the method ASTM D-6584.

RESULTS AND DISCUSSION

Experimental runs carried out at temperatures of 350 °C and 375 °C, pressures up to 300 bars and residence times up to 10 minutes were not satisfactory because a solid phase remained in the biodiesel sample and a strong decomposition was evidenced in the brownish color and pungent odor. The solid phase corresponds to unreacted chicken fat triglycerides, tripalmitin mainly, which is solid at room temperature conditions. This solid phase disappeared at temperatures of 400 °C and molar ratios higher than 6. Figure 1 shows the biodiesel (up) to glycerol (down) phase volume ratio with residence time at 400 °C, 200 bar and a 6:1 molar ratio.

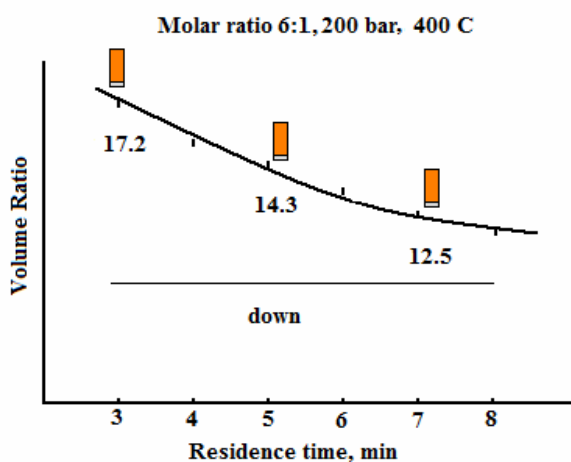


Figure 1. Biodiesel to glycerol phase volume ratio at experimental conditions: 400 °C, 6:1 and 200 bar

In Figure 1, a methyl esters analysis of biodiesel samples obtained at 5 minutes and 3 minutes showed the biodiesel yield increased with residence time. However, the sample taken at 7 minutes showed a lower yield than the previously taken at 5 minutes. This indicates methyl esters decomposition is taking place due to the longer residence time at these process conditions. A physical analysis of these samples showed a brownish color related to decomposition. The apparent decomposition could be attributed to the low excess methanol. If methanol is not in an enough excess to guarantee the existence of the supercritical phase at the proposed reaction conditions, instead of one homogeneous phase, there can be two phases: a

high temperature chicken fat phase and a supercritical methanol phase with the transesterification reaction taking place in the phase boundary. As observed in Figure 1 and as is usually observed in biodiesel production, a biodiesel and a glycerol phase were produced. However, at higher molar ratios, a second phase, which could not be glycerol due to the lower density in comparison to biodiesel, was obtained. Figure 2 shows the biodiesel (down) to second phase (up) volume ratio with residence time at 400 °C, 100 bar and a 9:1 molar ratio.

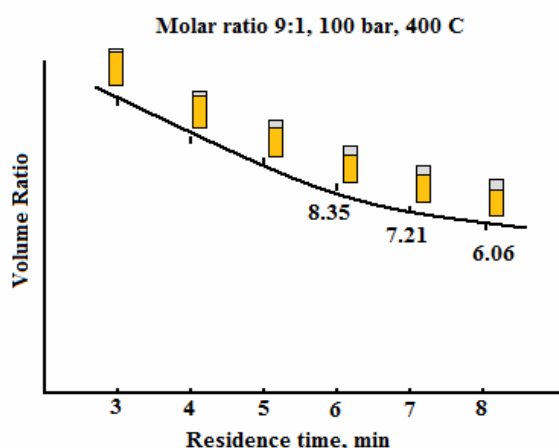


Figure 2. Biodiesel (down) to second phase (up) volume ratio with residence time at 400 °C, 100 bar and a 9:1 molar ratio.

In Figure 2, yield increased with residence time to 6 minutes and decrease with longer residence times. Biodiesel phase was analyzed to check for the decomposition products from methylesters. The decomposition of the unsaturated portion of methylesters in biodiesel has been reported even at temperatures as low as 300 °C [5,12,13,14], and has been associated to oxidation and transisomerization reactions [15] with formation of volatile products of the linear portion of the fatty acids [12]. Nevertheless, these decomposition products have not been positively identified in other studies. Iijima et al [9] reported the decomposition of methylesters of 16 and 18 carbons to shorter methylesters of 8 to 14 carbons, as well as the simultaneous glycerol decomposition in the supercritical transesterification of canola oil in the temperature range 400 to 450 °C and 40 MPa. These authors suggested that these shorter methylesters, which are also biodiesel, positively affect certain properties of the fuel such as viscosity and cold flow. As these shorter methylesters are not quantitated at these conditions a reduced yield is observed. A biodiesel sample obtained at 400 °C, 200 bar, molar ratio 9:1 and 8 minutes residence time was bubbled with nitrogen at 110 °C during 1 hour and the collected light fraction was analyzed by means of GC-MS. Table 1 summarizes the identified components [11].

As shown in Table 1, the methylesters of 16 and 18 carbons decomposition products are also methylesters of 8 to 14 carbons, saturated and unsaturated, as was suggested by Iijima et al [9], some linear alkanes usually present in regular diesel and some glycerol decomposition products. Although the unsaturated fraction decomposition of biodiesel is not desirable, a partial decomposition could be allowed if properties such as the viscosity and cold flow are improved. In this aspect, as shown in Table 2, some of these products have lower melting points and viscosity than methylesters of 16 and 18 carbons and could potentially improve the properties of the obtained flow.

Table 1. Peak identification in light fraction of biodiesel

Peak	Name	Formula	mp °C	bp °C
1	1,2 Propanediol, 3 methoxy	C ₄ H ₁₀ O ₃	N/A	220
2	2 Propanol, 1,3 dimethoxy	C ₅ H ₁₂ O ₃	N/A	172.6
3	6-Heptenoic acid methyl ester	C ₈ H ₁₄ O ₂	N/A	N/A
4	Methyl Enanthate	C ₈ H ₁₆ O ₂	-55	172
5	3-Octenoic acid methyl ester	C ₉ H ₁₆ O ₂	N/A	N/A
6	Methyl Caprilate (Octanoate)	C ₉ H ₁₈ O ₂	-30	193
7	8-Nonenoic acid methyl ester	C ₁₀ H ₁₈ O ₂	N/A	N/A
8	Methyl nonanoate	C ₁₀ H ₂₀ O ₂	-35	213
9	4-Decenoic acid methyl ester	C ₁₁ H ₂₀ O ₂	N/A	N/A
10	Tridecane	C ₁₃ H ₂₈	-5	234
11	Methyl Caprate	C ₁₁ H ₂₂ O ₂	-18	224
12	1-Tetradecene	C ₁₄ H ₂₈	-13	252
13	Tetradecane	C ₁₄ H ₃₀	5,5	253
14	Methyl Undecenate	C ₁₄ H ₂₂ O ₂	-27	247
15	Pentadecane	C ₁₅ H ₃₂	9,9	270
16	Sebacid acid dimethylester	C ₁₂ H ₂₂ O ₄	N/A	N/A
17	Myristic acid methyl ester	C ₁₅ H ₃₀ O ₂	18	323

Figure 3 shows the biodiesel to second phase (up) volume ratio with residence time at 400 °C, 200 bar and a 9:1 molar ratio. In this experiments the biodiesel phase was up at residence times up to 5 minutes and down at longer residence times. However, yield was higher with time at 200 bar than at 100 bar (Figure 2).

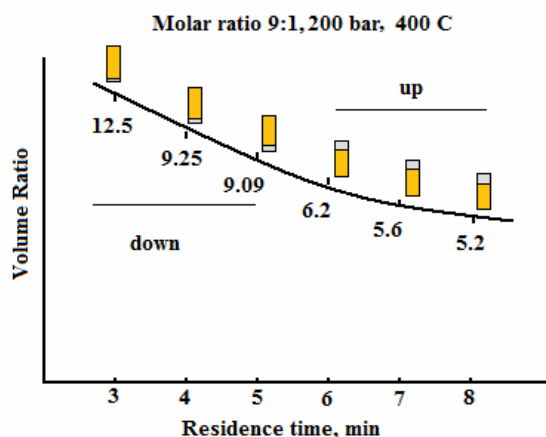
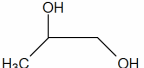
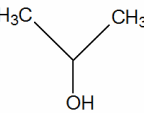
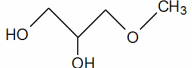
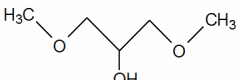
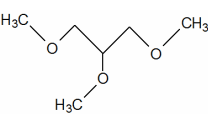
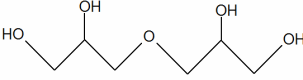
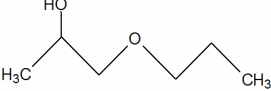
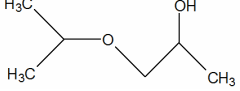


Figure 3. Biodiesel to second phase volume ratio with residence time at 400 °C, 200 bar and a 9:1 molar ratio.

An analysis of the second aqueous phase was performed by means of GC-MS in each of the samples shown in Figure 3. The second lower phase to residence times up to 5 minutes showed a prevalent composition of glycerol that decreases with increasing residence times, whereas samples with residence times longer than 5 minutes showed a low concentration of glycerol and the presence of several glycerol decomposition byproducts shown in Table 2.

Table 2. Identified glycerol decomposition products

Glycerol decomposition products	Name
	1,2 Propanediol
	2 Propanol
	1,2 Propanediol, 3 methoxy
	2 Propanol, 1,3 dimethoxy
	Propane, 1,2,3 trimethoxy
	Diglycerol
	2 Propanol, 1 propoxy
	2 propanol 1(1-methylethoxy)

In Table 2 is observed that the glycerol decomposition products include alcohols, glycerol ethers and polyglycerols such as diglycerol derived products. Some of these decomposition products, especially the most dehydrated ones, have a lower density than biodiesel and similar to that of methanol, which explains why the second phase is down when there is glycerol and up when glycerol decomposes. When comparing Figures 2 and 3, at low residence times the second phase is down at 200 bar. This could be attributed to the faster reaction rate at 200 bar, as indicated by the increased yield, which produces more glycerol than the glycerol that simultaneously decomposes. Some of these glycerol decomposition products have applications such as fuel additives and therefore could benefit properties of the fuel. However, this needs to be further assessed by means of a complete ASTM analysis.

CONCLUSION

Biodiesel production from chicken fat and methanol was effectively produced at supercritical conditions 400 °C, 200 bar (197 atm) and a 9:1 molar ratio. Due to the high temperature conditions of this process, methylesters and glycerol were decomposed. Methylesters decomposition produced short chain methylesters and linear alkanes, which are also fuel and therefore there is not yield loss. Some of these products have lower viscosity and

melting point than long chain methylesters and could potentially improve the quality of the obtained biodiesel. Glycerol decomposition produced several products due to methyl etherification and dehydration. Some of these products are well known fuel additives and could be blended with the biodiesel, with an increased yield in comparison to the conventional process. However, such possibilities need to be further assessed by means of a complete ASTM test.

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