

Depression of the Cloud Point of Biodiesel by Reaction over Solid Acids

Juan C. Yori, Miguel A. D'Amato, Javier M. Grau, Carlos L. Pieck, and Carlos R. Vera*

*Instituto de Investigaciones en Catálisis y Petroquímica—INCAPE—(FIQ-UNL, CONICET),
Santiago del Estero 2654, 3000 Santa Fe, Argentina*

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Biodiesel obtained by transesterification of soy oil with methanol was isomerized in the liquid phase at 125–275 °C using solid acid catalysts. The purpose of this work was to improve the cold flow properties of biodiesel by inhibiting the formation of crystals. Crystallization was analyzed by means of the measurement of the cloud point of the fuel. Tested catalysts were $\text{SO}_4^{2-}\text{-ZrO}_2$ and H-mordenite. At a temperature of reaction (T_r) lower than 125 °C, the catalytic activity was negligible. At $T_r > 200$ °C, the reaction rate was greatly accelerated, but the cetane number was also decreased and the amount of coke deposits was greatly increased. While reacting biodiesel at 150–200 °C, a small decrease (4–6.5 °C) of the cloud point was obtained without a meaningful decrease of the cetane index. Best results were obtained with $\text{SO}_4^{2-}\text{-ZrO}_2$ at 125 °C. Isomerization had both positive and negative effects on fuel properties: it reduced the cloud point but also increased the viscosity and decreased the cetane index. Due to the different reactivity between the saturated fraction (estearates, palmitates) and the unsaturated one (linoleates, linolenates, oleates), an adequate control of the degree of isomerization was only possible by performing a previous fractionation step. A good combination was obtained by reacting the saturates rich fraction at 200 °C over H-mordenite and the unsaturated rich fraction at 150 °C over $\text{SO}_4^{2-}\text{-ZrO}_2$. The fuel obtained by mixing both reacted fractions had a cetane index of 49.5 and a cloud point of –2 °C. However, this combined approach yields only a little benefit compared to those obtained with the single reaction over $\text{SO}_4^{2-}\text{-ZrO}_2$ at 125 °C.

Introduction

Biodiesel has lately emerged as an alternative fuel of wide acceptance because of its higher cetane number and lubricity and its lower environmental impact as compared to diesel petroleum fuels.^{1,4} Remarkable reductions in emissions other than nitrogen oxides^{2,3} and an increase in lubricity have been reported with neat biodiesel or biodiesel/diesel fuel blends. Biodiesel does not contain harmful aromatic hydrocarbons, and it does not produce sulfur oxides (SO_x). Particulate emissions are also decreased. Additionally, biodiesel has the appeal of being made from renewable resources and it is biodegradable.⁵ It can be produced by transesterification of soybean oil, rapeseed oil, canola oil, or other vegetable oils with methyl alcohol.^{6,7} Lard, tallow, and animal fats can also be transesterified, but their use is less common.⁸

The use of biodiesel is however limited despite its significant environmental benefits. The cost of producing biodiesel is greater than the cost of producing petrodiesel. Cold flow properties are also a concern when the temperature of operation goes below 10 °C. Problems with biodiesel often develop from

plugged fuel lines and filters, and these problems are caused by the formation of crystals. Methyl and ethyl esters of fatty acids have considerably higher crystallization temperatures than diesel fuel. Crystal growth inhibitors for diesel fuel, also known as pour point depressants (PPD), are available commercially.⁹ Though they have been reported to reduce the pour point of biodiesel, these additives usually do not reduce the cloud point nor improve the filterability of biodiesel at low temperatures.¹⁰ The use of PPD (e.g., polymethacrylate or ethylene vinyl acetate) admixed in levels of about 1–2% also increases the price of the fuel.

A comparison of typical cold flow properties, cold filter plug point (CFPP), pour point (PP), and cloud point (CP), shows that neat biodiesel (I) has a much poorer cold weather operability than petrodiesel (II): $\text{CFPP}^{\text{I}} = -10/-14$ °C, $\text{CFPP}^{\text{II}} = -31$ °C, $\text{CP}^{\text{I}} = -3$ °C, $\text{CP}^{\text{II}} = -17$ °C, $\text{PP}^{\text{I}} = -9/-16$ °C, and $\text{PP}^{\text{II}} = -24$ °C. Values of CFPP, PP, or CP are much higher for biodiesel, 15–20 °C over the values of petrodiesel. The importance of improving the low temperature properties of biodiesel then cannot be disregarded. Research in this field has lately appeared in the scientific and patent literature. Nouredini¹¹ proposed that the glycerol byproduct of the production of biodiesel could be etherified with isobutylene and the formed branched ether added to the biodiesel pool in order to produce a fuel with reduced viscosity and a cloud point below 0 °C. Lee et al.¹² winterized biodiesel in order to reduce its crystal-

* Corresponding author. Tel.: +54-342-4555279. Fax: +54-342-4531068. E-mail address: cvera@fiqus.unl.edu.ar.

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lization temperature. Winterizing was used in this case for the removal of the waxy palmitate fraction of biodiesel. This was not however an efficient way of removing the saturated methyl esters of high crystallization point because of the low yield of the separation process. Dry fractionation (with an emulsifying agent) of the crystals formed during chilling of fatty acid mixtures¹³ can also be used, but the yield is also not very high. Lee et al.¹⁴ have reported the reduction in the crystallization temperature of biodiesel by 7–14 °C by the use of branched alcohols in the synthesis of the methyl fatty acid esters of the fuel. Methyl, ethyl, propyl, isopropyl, 2-butyl, *tert*-butyl, and neopentyl esters were synthesized from soybean oil, canola oil, lard, and tallow. In all cases, the crystallization temperatures of the methyl esters were significantly higher than those of the branched esters. The authors themselves however disregarded the impact of this way of producing low pour point biodiesel, because of the high cost of branched alcohols. Also when branched alcohols are used in the alkali catalyzed transesterification, a lower rate is observed.

As indicated in recent studies,^{15,16} the cloud point is highly related to the fatty acid composition of biodiesel. High percentages of saturated fatty acids of long and linear chains are responsible for high cloud points. Skeletal branching of biodiesel is studied in this work as a simple means of improving its cold flow properties. The branching is supposed to disrupt the van der Waals interaction between the long straight chains of fatty acid methyl esters. In this way, the crystallization phase change can be shifted to lower temperatures. Isomerization has the appeal of not needing the addition of new compounds to the biodiesel pool or the use of expensive raw materials (like branched alcohols). Isomerization over solid acids has already been used for the skeletal branching of fatty acids¹⁷ with the purpose of depressing their crystallization temperature. In this case, the catalysts were acid clays and zeolites (H-mordenite, ALPO, and SAPO) and the temperature of reaction was 250–300 °C. The choice of the catalyst is important because for most of them deactivation is fast due to the formation of oligomers and coke. The acid catalysts tried in this work were SO_4^{2-} – ZrO_2 and H-mordenite. SO_4^{2-} – ZrO_2 is sometimes referred as a solid superacid because it has an acidity greater than 100% H_2SO_4 .¹⁸ It has the ability of isomerizing refractory short linear hydrocarbons such as *n*-butane at low temperatures,^{19,20} and it is a versatile catalyst for a wide variety of acid-catalyzed reactions.²¹ It has been successfully applied to the isomerization-cracking of paraffins in the carbon number range of diesel fuel.²² When operated at low temperatures, the formation of isomers is favored thermodynamically and the cracking and coking reaction rates are also decreased. To compare with the perfor-

Table 1. Properties of the Fresh, Untreated Biodiesel

| property | ASTM method | exp value |
|---|-------------|-------------|
| flash point, °C | D93 | 174.5 |
| cloud point, °C | D2500 | 5.2 |
| water and sediment (% vol) | D2709/D1796 | 0.03 |
| distillation temperature (90% vol, °C) | D86 | 336.6 |
| kinematic viscosity (cSt) (40 °C/100 °C) | D445 | 4.66/1.96 |
| ash (% mass) | D482 | 0.0136 |
| Conradson carbon residue (% mass) | D189 | 0.22 |
| calculated cetane index | D4737 | 55.92 |
| specific gravity (g/cm^3) | D1298 | 0.876 |
| base number (mg KOH/g muestra) | D664/D974 | 0.038/0.032 |
| sulfated ash (% mass) | D874 | 0.0202 |
| free/total glycerol (% mass) | D6584 | 0.03/0.03 |
| methanol (% mass) | GC | 0.145 |
| pour point (°C) | D97 | –3.0 |

mance of a zeolitic catalyst, an H-mordenite industrial isomerization catalyst was also tried.²³

Isomerization was performed in the liquid phase. The type of catalyst and the temperature of reaction were screened in order to obtain the optimum combination. As skeletal branching also decreases the cetane number, a minimum degree of branching in the biodiesel feedstock that could produce a meaningful decrease in the CP without decreasing the cetane number too much was desired. The catalysts were further characterized by temperature-programmed oxidation of coke deposits, sortometry, and X-ray diffraction (XRD).

Methods and Equipment

Materials. A reference batch of biodiesel fuel was prepared by a two-step batch procedure from degummed and refined soy bean oil. In the first step and after vacuum drying the oil at 80 °C and 0.3 atm, the oil was transesterified with methanol (6:1 alcohol:oil molar ratio) and NaOH catalyst (0.2%) in a stirred reactor (60 °C, 1 atm, 300 rpm stirring rate). After 1 h, the mixture was let to decant and the lower glycerol rich layer was removed. Conversion was about 85% as measured by gas chromatography with the method of Plank and Lorbeer.²⁴ In a second step, the upper ester layer was mixed with more methanol (0.2:1.0 alcohol:ester volume ratio) and catalyst (0.2%). In this second step (1 h, 60 °C), the transesterification was carried to completion. After the reaction, the methanol was vacuum flashed (70 °C, 0.3 atm) and the glycerol was removed by decanting. The biodiesel was then cooled to room temperature and passed through a column packed with Amberlyst 35W resin (5.4 meq g^{-1} , 2.0 meq mL^{-1} , moisture holding 57%, BET area 45 $\text{m}^2 \text{g}^{-1}$, pore diameter 250 Å) to remove dissolved sodium compounds, small amounts of glycerides and glycerol. The fuel was finally washed, centrifuged, and vacuum dried. After this treatment, the final base number (content of remaining NaOH) was negligible (see Table 1).

Catalysts. Zirconium hydroxide was prepared by precipitation of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Strem Chemicals, 99.99%) first dissolved in water. Ammonia was added dropwise until a pH of 10 was reached. The $\text{Zr}(\text{OH})_4$ gel formed was then filtered and dried overnight at 110 °C. The dried xerogel was sulfated by immersing it in a 2 N H_2SO_4 (10 mL $\text{g}_{\text{cat}}^{-1}$) solution for 1 h. Then, it was calcined in air (10 mL min^{-1} , 600 °C, 3 h). The thus produced SO_4^{2-} – ZrO_2 catalyst was dried overnight and finally ground and sieved to 35–80 meshes. Mordenite in the H form was supplied by Norton (Zeolon 900-H, 1/16 in. pellets). All the catalysts were used in the reaction in the form of particles sieved to 35–80 in order to eliminate filterability problems and the formation of suspensions of colloidal particulate material which could distort the measurement of the crystallization point.

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Fuel Properties. Both the pour and cloud points were measured according to the method described by the corresponding ASTM D97 and D2500 norms.²⁵ Due to the relatively inaccurate detection of the cloud point by visual inspection, three independent measurements were done and averaged to decrease the statistical error. The viscosity was measured in a Cannon–Fenske capillary glass calibrated viscosimeter and according to the ASTM D445 norm.²⁵ The viscosimeter with the sample was first immersed in an oil bath at 6 or 40 °C before performing each measurement. Cetane number was estimated by means of the distillation curve and the density of the fuel (ASTM D4737 method). Other properties, as detailed in Table 1, were determined according to the corresponding ASTM method.²⁵

Fractionation of Biodiesel. Vacuum-flashed (1 h, 70 °C, 0.3 atm), water-free biodiesel was put in a closed flask and slowly chilled to 0 °C during 3 h. The temperature was slowly decreased from room temperature at about 0.5 °C min⁻¹. The sample was maintained at 0 °C during 3 h, and then, the liquid upper phase was removed and placed in another flask. Both flasks were then allowed to warm to room temperature. These fractions were named the winterized saturated fraction (lower phase) and the winterized unsaturated fraction (upper phase).

Isomerization. Skeletal isomerization of the fatty acid methyl esters was performed in the liquid phase in an autoclave stirred reactor. The vessel and all connections were made of stainless steel. The reaction was carried out at 1 atm, with constant stirring (150 rpm), and at 125, 150, 200, 225, 250 and 275 °C. In all cases, a fixed amount of 2 g of catalyst ground to 35–80 meshes was used. In each experiment, 100 mL of fresh biodiesel was placed in the reactor and the system was heated to the target temperature in 20 min and under N₂ bubbling (5 mL min⁻¹) to remove traces of air. The reaction was carried out at the specified temperature for 60 min, and then, the reaction was quenched by cooling the reactor in an ice bath.

Kinetic Analysis. In order to assess the relative importance of the cracking and isomerization reactions, the composition as a function of reaction time was recorded in a experiment using a SO₄²⁻–ZrO₂ catalyst. The reaction temperature was 250 °C, and the total reaction time was 60 min. The rest of the conditions are the same as those detailed in the previous paragraph.

Chromatographic Analysis. Gas-phase chromatography was used in all cases. The mixture of products was analyzed with a simulated distillation column, and the products were lumped into boiling point cuts. A Supelco SimDis2887 capillary column was employed. For the same length of hydrocarbon chain and for the same amount of double bonds, branched products had a lower boiling point and were desorbed first. For the analysis of the components of the original nonisomerized biodiesel batch and for the analysis of the samples used in the experiment for the kinetic analysis, a DB-5 Phenomenex capillary column was used. The sample of biodiesel was derivatized with *N*-methyl-*N*-trimethylsilyl-trifluoro-acetamide (MSTFA) before injection.²⁴

Catalyst Characterization. The catalysts were characterized by different techniques. XRD spectra were recorded on Shimadzu XD-1 equipment, using Cu K α radiation filtered with Ni. The specific surface area was measured by adsorption of nitrogen at the temperature of liquid nitrogen by the BET method with a standard static volumetric equipment (Quantachrome NOVA-1000). The carbonaceous deposits formed on the catalysts during the reaction were analyzed by temperature-programmed oxidation (TPO). Combustion products were transformed into CH₄ in a methanator and then analyzed in a flame ionization detector (FID).

Results

Table 1 shows the property values relevant to the fuel performance of the original biodiesel sample. No mono-, di-,

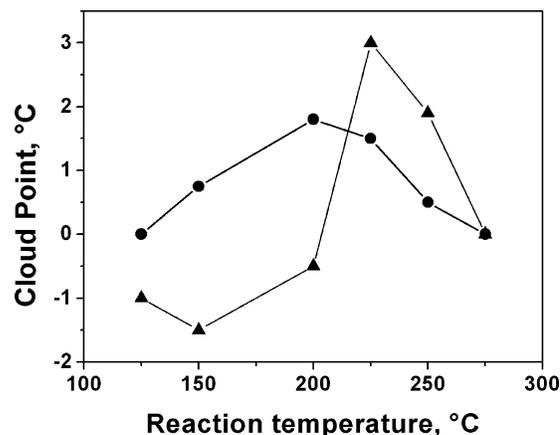


Figure 1. Cloud point of samples isomerized over HM (●) and SZ (▲): influence of reaction temperature.

or triglycerides were detected. Yu et al.²⁶ have found that glycerides amounts as small as 0.1% increase the cloud point, though they do not seem to affect the pour point. The distribution of fatty acids (in mass %) as determined by gas chromatography was: palmitic (10.2%), stearic (3.7%), oleic (23.2%), linoleic (54%), and linolenic (8.9%). The saturated fraction as determined by this method was 14%.

The SO₄²⁻–ZrO₂ catalyst (SZ) had a specific surface area of 110 m² g⁻¹ after being calcined at 600 °C. It also had an average Wheeler pore radius of 27 Å and a pore volume of 0.14 mL g⁻¹. The analysis by XRD showed that the catalyst had a mainly tetragonal structure, the catalytically active phase of this catalyst. Inspection of the peaks at 2 θ = 30.5° and 28.2° due to the tetragonal (active) and monoclinic (inactive) phases indicated that the volume fraction of the tetragonal fraction was higher than 90%. The H-mordenite catalyst (HM) had a specific surface area of 515 m² g⁻¹, an average Wheeler pore radius of 16 Å, and a pore volume of 0.40 mL g⁻¹. The XRD spectrum corresponded to mordenite crystals dispersed over a bohemite matrix.

Figure 1 shows the cloud point (CP) values of the samples isomerized at different reaction temperatures (T_r). The CP of the isomerized samples was always lower than that of the unreacted biodiesel sample (5.2 °C), but the variation with T_r was not uniform. An optimum temperature (minimum CP) was found for SZ at T_r = 150 °C, while for HM, the optimum was located on the extremes of the scanned temperature range, T_r = 125 and 275 °C. The variation was not monotonic, and this effect was attributed to the concurrence of reactions of oligomerization. The oligomers present in the liquid mixture would increase the CP, and those remaining on the surface would polymerize and deactivate the catalyst, due to the blocking of the acid active sites. Carbon deposits in growing amounts as the reaction temperature was increased were detected over both catalysts (see Figure 4).

The results of the temperature-programmed-oxidation tests performed over the used catalysts (Figure 2) indicate that the coke deposits are mainly formed by an adsorbed fraction, slightly polymerized, which is desorbed or burnt at 150–450 °C and which can be easily removed by washing with acetone. The rest of the coke has a higher degree of polymerization and cannot be extracted with acetone. This coke is burnt with a maximum rate at 500 °C in the case of SZ and at 550 °C in the case of HM. The temperature difference between the two TPO

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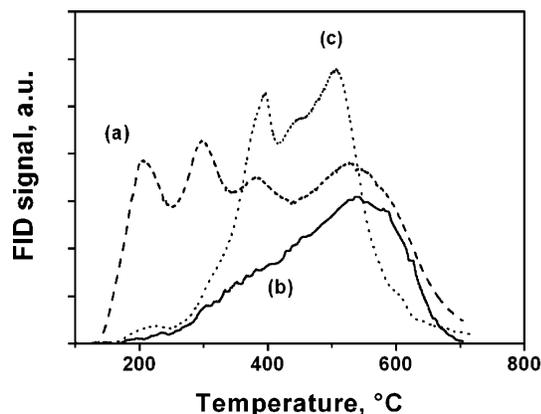


Figure 2. Temperature-programmed oxidation of the coke deposited over the catalysts during the isomerization reaction: (a) HM ($T_r = 200$ °C); (b) HM ($T_r = 200$ °C) rinsed with acetone; (c) SZ ($T_r = 275$ °C) rinsed with acetone.

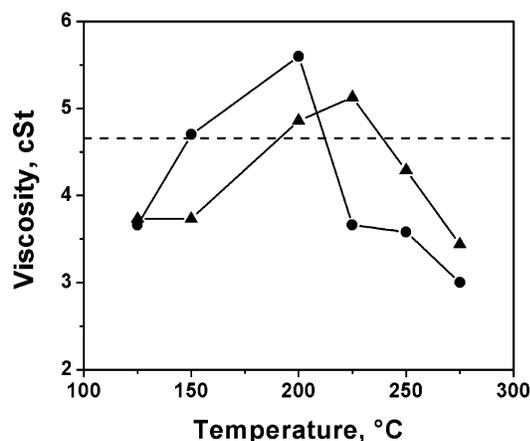


Figure 3. Viscosity at 40 °C of biodiesel samples isomerized over HM (●) and SZ (▲): (dotted line) viscosity of the original biodiesel sample.

maxima can be attributed to a higher degree of polymerization of the coke on HM. The position of the TPO maxima were almost independent of the reaction temperature. The amount of carbon (in mass %) was 2.6–2.8% for both catalysts of Figure 2.

Results corresponding to the influence of isomerization on viscosity can be seen in Figure 3. A similar effect as that seen in Figure 1 was found, i.e., a nonmonotonic pattern of variation. The viscosity of the isomerized samples was in most cases smaller than that of the original biodiesel sample. First, a viscosity increase is found when increasing the temperature, but this trend is reversed at temperatures higher than 200–250 °C. The minimum viscosity was found at a relatively high temperature, $T_r = 275$ °C, for both catalysts. The decrease below the original value can be attributed in this case to the cracking of long chain molecules into smaller chain ones with lower specific viscosity.

The amount of carbon on the catalysts increased as the reaction temperature was raised, as is seen in Figure 4 for the $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst. The amount of carbon deposits is negligible after the reaction at 125 °C but is very high, almost 3%, when the reaction is performed at 275 °C. The latter amount is higher than that found during isomerization of short chain alkanes (1–1.5%),²⁷ but as was seen in Figure 2, much of it has a low polymerization degree and it can be easily removed.

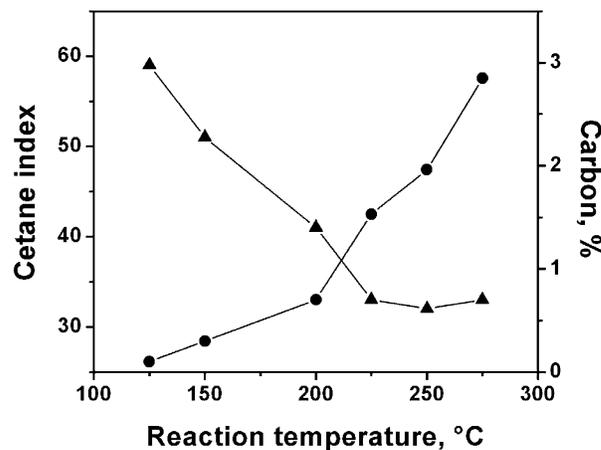


Figure 4. Cetane index (▲) and percentage of carbon deposited over the catalyst (●) with SZ catalyst.

Table 2. Properties of Winterized Biodiesel, Isomerized and Nonisomerized

| fraction | cloud point [°C] | cetane index |
|--|------------------|--------------|
| total, untreated | 5.2 | 55.9 |
| unsaturated (liquid at 0 °C) | 3.0 | 52 |
| saturated (solid at 0 °C) | 5.5 | 58 |
| A: unsaturated/isomerized (150 °C, SZ) | -3.0 | 50 |
| B: saturated/isomerized (200 °C, HM) | 0.5 | 49 |
| B: saturated/isomerized (200 °C, SZ) | -0.5 | 45 |
| A + B | -2.0 | 49.5 |

The cetane index had a smoother variation as a function of temperature (see Figure 4). Isomerization had a clear negative effect over the cetane index. Branching reduces the boiling point and therefore also the cetane index. At this point, some reflection over the nature of the different fractions of biodiesel and their reactivity seems relevant. The saturated fraction (estearates and palmitates) contains no reactive double bonds and therefore comprises the less reactive mixture for isomerization. Conversely, the unsaturated fraction (oleates, linoleates, and lino-leolates) should react easily due to the easier formation of adsorbed carbenium ions on the surface of acid catalyst sites, by attack on sp^2 carbons. For a same degree of conversion, higher temperatures should be needed for the saturated fraction and lower temperatures for the unsaturated one. This reactivity mismatch made us think on the convenience of fractionating biodiesel before reaction, to react them under different conditions and mix them afterward.

Many researchers^{28–30} have reported that the cetane number (CN) of biodiesel depends on the composition of the source oil. The more saturated and longer the fatty acid in the oil, the higher the CN of biodiesel. The most influencing factor is the unsaturation degree, and it has been shown that $\text{CN}(\text{octadecane}) > \text{CN}(\text{methyl estearate}) > \text{CN}(\text{methyl palmitate}) > \text{CN}(\text{methyl oleate})$. The results related to the isomerization of fractionated biodiesel are included in Table 2. The solid fraction winterized at 0 °C comprised 29% of the original volume. The much higher percentage with respect to the saturates content determined by chromatography (14%) was attributed to the low efficiency of the crystallization method. The chromatographic analysis indicated that a high percentage of oleates were coprecipitated during winterization.

Due to the higher reactivity of the unsaturated fraction, this was reacted at a low temperature, over the catalyst that had the

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best low-temperature activity, SZ. A temperature of 150 °C was chosen. A meaningful decrease of the cloud point was obtained with a small decrease of the cetane index (see Table 2). In the case of the saturated fraction, a reaction temperature of 200 °C was used and both the SZ and the HM catalyst were tried. The results indicate that a higher decrease of the CP is obtained by using SZ but the decrease of the CI is prohibitively high. In the case of HM, the CP decrease was lower but the loss of cetane points was more acceptable. The best solution was found after mixing the fractions after isomerization because the overall CP was -2 °C. The resulting cetane index (CI = 49.5) was similar to the minimum established by the strict standard for biodiesel (CI = 49). If these results are compared with those obtained by isomerizing the whole biodiesel sample over $\text{SO}_4^{2-}\text{-ZrO}_2$ at 125 °C, it can be seen that the latter produces a similar value of cloud point, a lower viscosity, and a higher resulting cetane index. Therefore, the fractionation scheme seems not convenient.

With respect to the reasons for the cloud point shifts seen, these were attributed both to isomerization and cracking reactions though a clear discrimination between the two was difficult due to the high complexity of the mixtures. The SimDis distillation curves were an envelope of many peaks but they indeed displayed a shift of the mean and a broadening of the boiling curves corresponding to the treated samples in comparison to the curve of the blank (see Figure 5). It is known that for equal carbon numbers branched isomers are boiled first and desorb first from nonpolar silica columns such as that used in the SimDis tests.

An approximate kinetic analysis was performed by recording the composition of the solution at different reaction times. While oligomerization and cracking products could be separated by gas chromatography (ZB-5 column), this was more difficult in the case of isomerization products. Mostly, C_{18} unsaturated FAME suffered skeletal branching and the gas chromatography (GC) peak of branched C_{18} was always merged with the peak of linear C_{18} . It was evident that in reacted biodiesel samples there was a broadening and a shift of the peak of unsaturated C_{18} to lower temperatures. However, the quantification of the peak of branched compounds was only possible in the runs at the highest temperatures which produced a bigger peak (shoulder) of branched C_{18} . The results corresponding to the reaction of biodiesel over $\text{SO}_4^{2-}\text{-ZrO}_2$ at 250 °C are included in Figure 6. A simple kinetic model with lumped components was used and the value of the kinetic constants was obtained:

$$\frac{d[\text{C}_{18}^{\text{=}}]}{dt} = -k_1[\text{C}_{18}^{\text{=}}] - k_3[\text{C}_{18}^{\text{=}}][\text{CRACK}] \quad (1)$$

$$\frac{d[\text{CRACK}]}{dt} = -k_2[\text{ISO}] - k_2[\text{C}_{18}^{\text{=}}][\text{CRACK}] \quad (2)$$

$$\frac{d[\text{ISO}]}{dt} = -k_1[\text{C}_{18}^{\text{=}}] - k_2[\text{ISO}] \quad (3)$$

$$\frac{d[\text{OLIGO}]}{dt} = -k_3[\text{C}_{18}^{\text{=}}][\text{CRACK}] \quad (4)$$

The concentration of each species is marked with square brackets. The mass balance indicated that in this experiment the fraction of palmitic and stearic methyl esters remained practically constant and that the unsaturated fraction was mainly reacted. Four compositional lumps were used to describe the system: $\text{C}_{18}^{\text{=}}$ = (oleic, linoleic, and linolenic esters), CRACK = (cracking products), ISO = (branched $\text{C}_{18}^{\text{=}}$), OLIGO = ($\text{C}_{n-1}\text{COOCH}_3$, $n > 18$). A better description was not possible

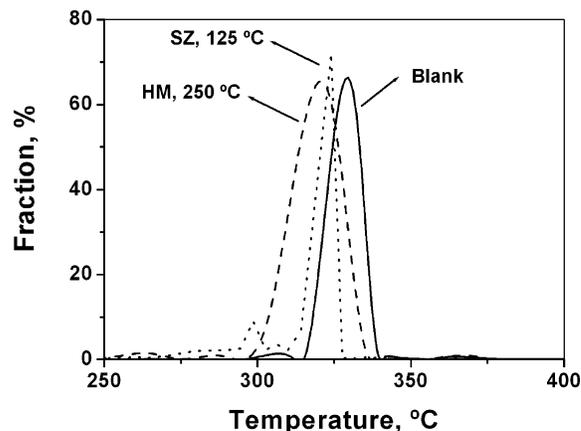


Figure 5. Comparison of the SimDis curves of the original biodiesel sample (blank) and two treated samples.

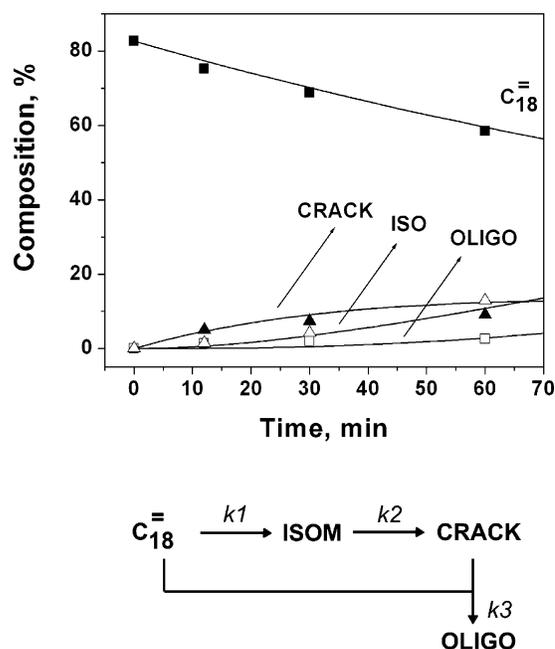


Figure 6. Reaction of biodiesel over $\text{SO}_4^{2-}\text{-ZrO}_2$ at 250 °C: composition as a function of time. The proposed simplified reaction network with compositional lumps is as follows: $\text{C}_{18}^{\text{=}}$ = oleic, linoleic, and linolenic esters; CRACK = cracking products; ISO = branched $\text{C}_{18}^{\text{=}}$; OLIGO = $\text{C}_{n-1}\text{COOCH}_3$, $n > 18$.

due to the limitations of the GC analysis. The fitted values of the constants were the following: $k_1 = 0.0055$, $k_2 = 0.022$, and $k_3 = 0.00018 \text{ min}^{-2}$ (when concentration is expressed in mass %). According to their position in the chromatogram, ISO seemed to be mainly composed of monobranched (methyl, ethyl) fatty acid methyl esters (FAME) with unsaturated C_{18} acid chains. CRACK products were $\text{C}_8\text{-C}_{10}$ fatty acid methyl esters or hydrocarbons. Oligomerization products were esters with C_{19-20} acid chains. Heavier compounds did not appear in the chromatogram, and it was supposed that if they were formed during the reaction they remained as coke on the catalyst. Even at the high temperature of 250 °C, at the end of the run the yield of isomerization products is more important than the yield of cracking products. The ISO/CRACK ratio is supposed to be further increased at lower temperatures.

Conclusions

Skeletal isomerization of biodiesel at low temperatures (125–150 °C) can be achieved by means of the reaction over catalysts

of high acid strength like H-mordenite and $\text{SO}_4^{2-}\text{-ZrO}_2$. At temperatures equal to or higher than 200 °C, the coking of the catalysts is too high. Isomerization has both positive and negative effects on the fuel properties. On one side, it reduces the cloud point, but on the other, it reduces the cetane index.

Due to the different reactivity of the fraction rich in saturated methyl esters (estearates, palmitates) and the fraction rich in unsaturated ones (linoleates, linolenates), if the reaction is performed on the crude biodiesel, it is difficult to achieve a good control of the isomerization degree and the cetane index is excessively depressed. Better results are obtained by fractionating the biodiesel first and isomerizing the fractions under different reaction conditions, mild for the unsaturated fraction and severe for the saturated one. A good combination was found in this work by isomerizing the unsaturated fraction at 150 °C

over $\text{SO}_4^{2-}\text{-ZrO}_2$ and the unsaturated fraction at 200 °C over H-mordenite. The biodiesel obtained in this way had a cloud point of -2 °C and a cetane index of 49.5. However, the benefit obtained by lowering the cloud point seems to not justify the loss in cetane index and the addition of process steps. In general, it must be concluded that though isomerization depresses the CP to some extent it produces an unacceptable decrease of the cetane index.

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