

Zirconium Sulfate as Catalyst for Biodiesel Production by Using Reactive Distillation

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ABSTRACT

Production of fatty acid esters (biodiesel) from oleic acid and 2-ethylhexanol using sulfated zirconia as solid catalyst for the production of biodiesel was investigated in this work.

The parameters studied were temperature of reaction (100 to 130°C), molar ratio of alcohol to free fatty acid (1:1 to 3:1), concentration of catalyst (0.5 to 3%wt), mixing speed (500 to 900 rpm) and types of sulfated zirconia (i.e modified, commercial, prepared catalyst according to literature and reused catalyst). The results show the best conversion to biodiesel was 97.74% at conditions of 130°C, 3:1, 2wt% and 650 rpm using modified catalyst respectively. Also, modified catalyst gave identical results to that of commercial one. Simulation study was adopted from basic principles of reactive distillation and the results were close to an acceptable degree.

Keywords: biodiesel, reactive distillation, sulfated zirconia, heterogeneous catalyst

كبريتات الزركونيوم كعامل مساعد لأنتاج البايوديزل بأستخدام التقطير التفاعلى

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الخلاصة

في هذا البحث تم دراسة أنتاج البايوديزل باستخدام التقطير التفاعلي خلال تفاعل حامض الأوليك مع كحول ٢ – أثيل هكسانول واستخدام كبريتات الزركونيوم كعامل مساعد صلب. مثل هذه العوامل المساعدة يمكن فصلها بسهولة من محلول التفاعل واعادة استخدامها مرة أخرى وليس كما في العوامل المساعدة السائلة وكذلك ممكن أستخدامها في العمليات المستمرة. على الرغم من أن كفاءتها أعلى من السائل الا انها مستخدمة في السنوات الاخيرة.

المتغيرات التي تم دراستها هي درجة حرارة التفاعل النسبة المولية للكحول الى الحامض الشحمي تركيز العامل المساعد سرعة الخلط طرق مختلفة لتحضير كبريتات الزركونيوم. أظهرت النتائج ان أعلى تحول يصل ال ٩٧.٧٤% عند ظروف ١٣٠ م، ٣:١٦ ٢٢ وزنا ٢٠٥ دورة/دقيقة عند أستخدام العامل المساعد المحسن. كذلك أظهرت النتائج أن التجاري أقرب الى العامل المساعد المحسن. تم أيضا دراسة محاكاة لنتائج التقطير النفاعلي ولوحظ أن هناك تقارب بينهم.

الكلمات الرئيسية: بايوديزل، التقطير التفاعلي، كبريتات الزركونيوم، العوامل المساعدة الصلبة



1. INTRODUCTION

The synthesis of biodiesel has been receiving more attention all over the world since the raw materials (vegetable oils and animal fats) are often locally available, renewable, and environmental friendly. In addition, biodiesel can be used without modification of diesel engines Ma, and Hanna, 1999 and Gerpen, 2005. The transesterification of triglycerides (TGs) and esterification of free fatty acids (FFAs) contained in vegetable oils and animal fats are the two main reactions for converting vegetable oils and animal fats into biodiesel. Biodiesel is currently produced in batch processes which are penalized by important shortcomings such as: high alcohol demand required to shift equilibrium towards fatty esters, necessity of catalyst neutralization causing a salt waste stream, high separation costs of fatty ester products from the reaction mixture, high costs caused by complex processes including multiple reactors and separation units Meng, et al., 2009, Kiss, et al., 2008 and Omota, et al., 2003. As a result, process intensification technologies like reactive distillation have become more attractive in recent years, Noshadi, et al., 2012. Reactive distillation (RD) is a well-known example of process intensification, in which chemical reaction and thermodynamic separation occur at the same time and in the same place of the column, Keller, et al., 2011. In comparison to conventional reactor-separator sequences, RD allows for higher reactant conversion, product selectivity and energy savings with favorable investment and operating costs. However, there are several constraints that limit the successful application of RD, such as complex design, difficult scale-up and advanced process control, Schoenmakers and Bessling, 2003. Reactive distillation can be effectively used to improve the selectivity of a reaction especially when an intermediate product is desired in the series or combination of series and parallel reactions. Removing one of the products from the reaction mixture or maintaining low concentration of one of the reactants can lead to reduction in the rates of side reactions, Vinay, et al., 2013.

Use of solid acid catalysts can also greatly improve the economics of biodiesel synthesis because of their ability to be reused and the decreased need for many separation steps. In particular, solid acid catalysts can carry out transesterification and esterification simultaneously using low cost feed stocks without multiple reaction and post-treatment steps, greatly improving the economics of biodiesel production, Lotero, et al., 2005, Furuta, et al., 2004, Suwannakarn, et al., 2009 and Garcia, et al., 2008. Heterogeneous catalysis for biodiesel production has been extensively investigated in the last few years. The catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume and active site concentration, Smith, et al., 2006. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acidity, i.e. they behave as electron acceptors, and negative oxygen ions (anions) which behave as proton acceptors and are thus Brønsted bases. This has consequences for adsorption. Recently, sulfated zirconia (SO₄/ZrO₂) catalysts have found many applications in several acid catalyzed reactions, Arata, et al., 2003. These compounds are active for hydrocarbon conversion at temperatures lower than the most of the generally used solid catalysts, normally at temperatures from 100 to 200°C or lower, Ardizzone, et al., 1999. S-ZrO₂ is promised as an active catalyst for esterification due to its high acid strength.

The aim of this work is the study of the production of biodiesel in a reactive distillation column using zirconium sulfated as heterogeneous catalyst at different process conditions: temperature, oleic acid: 2-ethylhexanol ratio, catalyst concentrations and different preparation methods of sulfated zirconia.



2. EXPERIMENTAL Work

2.1 Materials

Oleic acid (purity 98%) was supplied from Thomas baker, india. 2-Ethylhexanol alcohol (purity 99% from GC analysis) was maintained from Ministry of Science and Technology as industrial alcohol. Since this alcohol is typically a waste alcohol from the manufacturing of butanol, this process makes sense from an economic viewpoint. Zirconium oxychloride and sulfuric acid was used for preparing zirconium sulfate as catalyst, ethanol and phenolphthalein for titration.

2.2 Reaction Procedure

The reaction was carried out in a lab scale reactor with a volume of 250 ml. The fatty acid was fed into the reactor in order to be preheated it before the catalyst and the alcohol were added. When the desirable reaction temperature was reached, the catalyst and the alcohol were adjoined into the reactor and the reaction started. The stoichometry amount of molar ratio alcohol:oleic acid is 1:1; however, since we are on the presence of an equilibrium reaction, a higher amount of alcohol should be used in order to display the reaction towards the desirable product. The withdrawn samples, taken at specific established times, allowed to cool and then centrifuged to separate out any catalyst particles to limit further reaction. After that was analyzed by a titration procedure to measure the residual acidity. A weighted amount of the sample was dissolved in ethanol; a few drops of phenolphthalein were added as indicator. A 0.1 N alkaline solution of KOH was used to perform the titration. The amount of KOH consumed was registered and the acidity was calculated using the following equation:

$$a = \frac{V \times 1000 \times Mwt. \times C}{W}$$
(1)

where a: acidity index; V: volume of KOH solution employed for titration, ml; Mwt..: molecular weight of KOH, g/mol; C: concentration of the solution used for titration, mol/l; W: weight of the sample taken to analyzed, g.

Using Eq.(2), the conversion of free fatty acid (X) was calculated:

$$X = \frac{a_i - a_t}{a_i} \tag{2}$$

Where a_i is the initial acidity of the mixture and a_t is the acidity at "t" time.

2.3 Preparation of Zirconium Sulfate (SZ)

(a) Preparation of SZ by the Solvent-Free Method

SZ by the solvent free method (SF) was prepared by grinding $(NH_4)_2SO_4$ and $ZrOCl_2.8H_2O$ at a molar ratio of 6:1 in an agate mortar for 20 min at room temperature. After that calcined at 600°C for 5 h, **Sun, et al., 2005**.

(b) Preparation of SZ by the Conventional Method

Zirconium oxy-chloride (ZrOCl₂.8H₂O) of 20 g was dissolved in 200 ml water, then the solution reached to pH of 9 using 25% w/w NH₃ solution and constant mixing to permit zirconium hydroxide to precipitate. The precipitation of zirconium hydroxide was washed to



remove chloride salts, then filtered with a Buchner funnel. In the next step, the zirconium hydroxide was dried for 24 h at 100°C and impregnated with 1 M H₂SO₄ under constant mixing for 30 min. Then, the SO_4^{2-}/ZrO_2 was dried at 100°C for 24 h and calcined in air for 3 h at 650°C, **Yadav** and **Nair**, **1999**.

(c) Preparation of Modified SZ Catalyst

50 g of zirconium oxychloride ($ZrOCl_2.8H_2O$) supplied from local market was dissolved in 500 ml water, then zirconium hydroxide allowed to precipitate at pH of 9 using 25% w/w NH₃ solution under constant mixing for 30 min. The white precipitation was washed with water to remove the chloride salts until the pH of the solution reached 7, then filtered with conical funnel.

In the next step, the zirconium hydroxide dried at 110° C for 18 h, then impregnated with 1 M H₂SO₄ under constant mixing for 8 h. After precipitation for 24 h, the SO₄/ZrO₂ was dried for 24 h at 110° C and then calcined in air for 3 h at 650° C.

3. PROCESS SIMULATION

The UNIQUAC model was applied to consider the nonideal liquid- phase behavior. The degree of deviation from ideality in liquid phase is represented by γ_i (activity coefficient). It was employed for the vapor–liquid equilibrium (VLE) calculations in MATLAB.

Activity coefficient consists of two terms, residual and combinatorial

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{3}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right)$$
(4)

$$\ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k} \right) \right]$$
(5)

The process simulation software, Matlab R2011, was used in this work. The main processing unit include a reactive distillation column with 4 stages. The first column stage is the condenser and the fourth stage is the reboiler. The same experimental conditions were used in the simulation process. Composition was obtained on all stages assuming very small reflux ratio using the following equations, **Zapata**, et al., 2012:

• **For Condenser** (k =1, i=1-4))

$$\frac{dx_{1(i)}}{dt} = \frac{V_{(1)}y_{2(i)} - L_{(1)}x_{1(i)}}{H_{(1)}}$$
(6)

• For Column (k =2,3 and i=1-4)

$$\frac{dx_{k(i)}}{dt} = \frac{V}{M_{in}} \left(y_{k+1(i)} - y_{k(i)} \right) + \frac{L}{M_{in}} \left(x_{k-1(i)} - x_{k(i)} \right)$$
(7)

• For Reboiler (k=N and i=1-4)

$$\frac{dx_{N(i)}}{dt} = \frac{(L_{(k)}x_{N-1(i)} - V_{(k)}y_{N(i)})}{H_{(k)}} + \text{Rate of reaction}$$

$$Where$$

$$H = \text{holdup}$$

$$K = \text{stage}$$

$$(8)$$



i = component

Equilibrium ratio (k=2 to N)

$$\mathbf{y}_{\mathbf{k}(i)} = \frac{\alpha_i x_{k(i)}}{\sum_{j=1}^i \alpha_j x_{k(j)}}$$

Where α_i is the relative volatility x is composition of liquid phase y is composition of vapor phase

4. CHARACTERIZATION OF MODIFIED CATALYST

4.1 X-Ray Diffraction (XRD)

The powder X-ray diffraction patterns of sample was recorded using a Shimadzu XRD-6000 diffractometer with Ni filtered CuK α radiation ($\lambda = 0.154$ nm) in the range of $2\theta = 10-60^{\circ}$. It has been generally realized that the crystalline phase of the SZ catalysts plays a very important role in catalytic activity and zirconia with tetragonal structure showing a higher catalytic activity than that of monoclinic ZrO₂. **Fig. 1** displays the XRD for S/ZrO₂. The S/ZrO₂ sample reveal well crystalline structure. The phase shown for sulfated zirconia was orthorhombic at $2\theta = 25.35$, 27.59, 29.55, 32.88 and 36.32°.

4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 2 shows FTIR of sulfated zirconia. The band at 1332.72cm⁻¹ is due to the splitting of the S=O asymmetric stretching, which implies the existence of sulfate species. While the band at 790 and 710 due to S-O stretching vibration. The bands at 1138 and 1267.14cm⁻¹ are normally stands for chelating bidentate sulfate ions coordinated to the zirconium cation. The peaks of t-ZrO₂ has also been observed at 649.97, 613.32, 588.25cm⁻¹.

4.3 Thermal Gravimetric Analysis (TGA)

The TGA/DTA analysis was performed with an EXSTAR 6000 series instrument and shown in **Fig. 3**. A 34.541 mg of sample was heated in the air (20 °C/min) from 50 to 900 °C. The weight loss and heat flow were measured as a function of temperature. Thermal analysis results for SZ catalyst after calcination was depicted in **Fig. 3**. TGA showed that SO_4/ZrO_2 was thermally stable. There was no weight loss observed from 50 to 670°C but for higher temperature 670-800°C weight loss approximately 20% due to decomposition of sulfate. The beak in DTA curve due to phase transition hence, the sample was calcinated at 650°C.

4.4 Scanning Electron Microscopy (SEM)

The SEM of SO_4/ZrO_2 is shown in **Fig. 4**. The SEM of SO_4/ZrO_2 showed that the surface of ZrO_2 was distinctly altered, exhibiting considerable surface shining after sulfation. SEM images taken at higher magnification clearly showed the alternation and shining of the surface. This may be due to the presence of highly charged species, i.e. sulfate ions.

The textural properties were determined from the nitrogen adsorption isotherm determined after degassing at 200°C under vacuum at 5 - 10 mbar. The surface area was calculated using the

(9)



Brunauer–Emmett–Teller (BET) equation and the pore volume was determined at a relative pressure of 0.98. The most important results are given in **Table 1**. In principle, the specific surface area depends on the calcination temperature.

5. RESULTS AND DISCUSSION

5.1 Effect of Mixing Speed

Fig. 5 illustrates the variation of conversion with time at different mixing speeds varied from 500 to 900 rpm keeping other variables constants, temperature of 130°C, the molar ratio of acid:alcohol of 1:1 and concentration of SZ catalyst of 2wt%.

The results indicate the conversion of oleic acid increased from 64.64% at 500 rpm to 75.63% at 900 rpm to reach high value 90.16% at speed 650 rpm after 60 min reaction time. Increasing the mixing speed could tremendously shorten the reaction time, but for high speed inverse effect can be seen because droplet became very small rigid sphere and its surface cannot renewal. Conversions at end of reaction time (after 120 min) were 82.74%, 91.4% and 86.39% for 500, 650 and 900 rpm speed respectively. There are probably two reasons that mixing speed can intensify the esterification catalyzed by SZ:

stirring promotes the mixing of oleic acid and 2-ethylhexanol; 2-ethylhexanol lies on the top of oleic acid without stirring. The 2-ethylhexanol and acid layers break up and the reactants forms droplets once stirring starts, **Stamenkovic, et al., 2007**.

Also, SZ is insoluble in the reaction mixture and stirring is needed to help the mixing of catalyst with the reactants and decreases the resistance to mass transfer.

5.2 Effect of Reaction Temperature

Fig. 6 illustrates the relationship between conversion and time at temperatures of 100, 110, 120 and 130°C for molar ratio of oleic acid:2-ethylhexanol of 1:1 and concentration of SZ was 2wt%.

There are sharp increasing in conversion between higher temperature (130°C) and lower temperature (100°C). The oleic acid conversion was 91.4% at 130°C after about 60 min while at 100°C the conversion reached 66.78% after 120 min at the same conditions. The higher temperature helps to destroy the bonds between fatty acid molecules and permit alcohol molecules to insert between in the presence of sulfated zirconia that have acidic active sites.

5.3 Effect of Alcohol to Free Fatty Acid Molar Ratio

Fig. 7 demonstrates the effect of molar ratio of alcohol to acid ranging from 1:1 to 3:1 on conversion with time at constant temperature of 130°C and concentration of sulfated zirconia was 2wt%. It can be clearly seen when ratio increased from 1 to 3, the conversion was found to increase from 91.4% to 97.74%. This increment can be explained by the fact that higher molar ratio increases the solubility of acid in 2-ethylhexanol and therefore allow a better contact between the species over the heterogeneous catalyst. Also, the viscosity of 2-ethylhexanol /oleic acid mixture decreases when the 2-ethylhexanol to oleic acid ratio increases. This is because of lower viscosity of 2-ethylhexanol in comparison to the free fatty acid. When the viscosity decreased, the impact of diffusion of the reactants towards the catalyst particles decreased, and hence improved the interparticle diffusion that led to higher conversion.



On further increasing of alcohol concentration, there is little difference of conversion between 1:2 and 1:3. This can be explained by competitive adsorption of reactants on catalyst. Further increasing alcohol in the reaction mixture, majority of the sites on the catalyst surface were occupied by alcohol molecules.

5.4 Effect of Catalyst Concentration

By increasing the amount of catalyst, the reaction rate, hence conversion after a certain time can be further increased. Thus sulfated zirconia is suitable for reactive distillation applications where high activity is required in a short time, **Kiss, et al., 2008**. The effect of SZ amount (0.5-3%wt) on the reaction at constant temperature of 130°C and molar ratio of oleic acid :2-ethylhexanol of 1:1 was studied, and the results are shown in **Fig. 8**.

Conversion increased as time increase for all concentration and also increase as concentration of catalyst increase but it take different time to reach best conversion, for example at High concentrations the conversion achieved were 81.7%, 86.35% and 87.5% at 1%, 2% and 3% wt concentration respectively after 45 min reaction time. While for low concentration 0.5% wt more time needed to reach conversion of 79.74% after 90 min.

At low catalyst amounts, there were not enough active sites for the reaction. After 45 min the conversion for catalyst amount 2% wt was nearly the same that for 3% wt this may be due to blocking of active site, **Patel, et al., 2013**, poisoning, pore fillings or combination of these deactivation mechanism, **Lopez, et al., 2008**. In the same figure, can be seen there is a sharp difference in final conversion for catalyzed and non catalyst reaction, conversions were 91.4%, 84.9% and 49.88% for 2%, 0.5wt% and no catalyst respectively after 120 min reaction. The reaction without catalyst is very slow is start with 39.4% and end with 49.88% after 120 min.

5.5 Effect of Catalyst Preparation Method

According to preparation method, SZ activity effect the esterification reaction. The performance of various SZ was tested at constant reaction temperature of 130°C, alcohol:acid of 3:1, concentration of SZ of 2wt% and mixing speed of 650 rpm. The results depict in **Fig. 9**.

For oleic acid and 2-ethylhexanol, modified SZ was prepared and compared with one prepared by conventional method and other prepared by free solvent method. The results display that modified SZ awarded better conversion than other types, and its activity is identical to commercial one which achieved conversion of 96% in short time, nearly 30 min while for other methods, the conversion of oleic acid was 75% and 65% for conventional catalyst and free solvent catalyst respectively at the same time. The activity of modified method may be due to the strength, number of sites and Bronsted acidity.

For reused catalyst, the activity was below that of the fresh catalyst, it gave 76.35% conversion after 60 min compared to 90.16% conversion for modified catalyst at the same duration time. The decrease in reaction rate may be attributed to sulfur leaching, pore filling and small population of active site may have been lost during deactivation.

5.6 Testing of Biodiesel Obtained from Oleic Acid

Biodiesel obtained from oleic acid for best experiment was analyzed by ASTM (American Standard for Testing Material). **Table 2** shows biodiesel from this experiment.



5.7 Simulation Results

The presentation for comparing experimental and theoretical results shown in **Figs. 10** and **11** at various conditions of molar ratio of alcohol: acid, reaction temperature and catalyst concentration of 2wt% for oleic acid esterification.

There are good agreement between predicted and experimental composition at condition of 2:1 molar ratio, reaction temperature of 130°C and concentration of sulfated zirconia of 2wt% as indicated in **Fig. 10** for oleic acid. While for stochimetric ratio of 1:1 lower agreement observed as shown in **Fig. 11**.

From **Figs. 12** and **13** for oleic acid-biodiesel compositions at stochimetric ratio of 1:1 and different temperatures of 100°C and 130°C with SZ catalyst concentration of 2wt% and 0.5wt%, there are significant difference occurring between experimental and theoretical composition for FFA and biodiesel. This may be due to non ideality have very negative effect on composition at this ratio.

6. CONCLUSIONS

- 1- The conversion increased with increasing time and temperature but at different duration of time to reach best conversion, it take 60 min to reach 84.57% and 90.16% for temperature 120°C and 130°C respectively. While for lower temperatures take more time to reach the best conversion.
- 2- The best molar ratio of alcohol to fatty acid was 2:1 and when increased this ratio less effect was shown.
- 3- There is sharp difference in conversion for esterification reaction with and without catalyst. Also as concentration increased higher than 2wt% the conversion decreased as a result of active site of catalyst was broken.
- 4- The best mixing speed of stirring was 650 rpm.

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NOMENCLATURE

- a= acidity, mg KOH/g_{FFA}
- N= concentration of KOH solution, mole/l.
- mwt.= molecular weight of KOH solution, g/mole.
- V= volume of KOH solution, ml.
- m= weight of sample, g.
- X= conversion, dimensionless.
- γ_i^{C} = combinational term for activity coefficient
- γ_i^R = residual term for activity coefficient





Figure 3. TGA of modified sulfated zirconia.



Figure 4. SEM of modified sulfated zirconia.





Time (min) Figure 5. Effect of mixing speed on conversion of oleic acid.

[**Operating conditions**:molar ratio of free fatty acid: alcohol was 1:1, reaction temperature 130°C and concentration of sulfated zirconia 2wt%]



Figure 7. Effect of Acid: Alcohol molar ratio on oleic acid conversion.

[**Operating conditions**: reaction temperature 130°C, concentration of heterogeneous catalyst 2wt% (SZ) and mixing speed 650 rpm]



Figure 6. Effect of temperature on oleic acid conversion.

[**Operating conditions**: molar ratio of alcohol:FFA 1:1, heterogeneous catalyst of concentration 2wt% (SZ) and mixing speed 650 rpm]





[**Operating conditions**: reaction temperature 130°C, molar ratio of 2ethylhexanol:oleic acid 1:1 and mixing speed 650 rpm] Number 1



Figure 9. Different types of SZ catalysts for oleic acid conversion.

[**Operating conditions**: molar ratio of oleic acid :2-ethylhexanol 1:3, reaction temperature 130°C, catalyst concentration 2wt% (SZ) and mixing speed 650 rpm]





Figure 11. mole fraction oleic acid and its biodiesel.

[**Operating conditions**: molar ratio of alcohol: acid of 1:1, reaction temperature 130°C and concentration of sulfated zirconia 2wt%]



Figure 10. mole fraction of oleic acid and its biodiesel.

[**Operating conditions**: molar ratio 2:1 (alcohol:acid), reaction temperature 130°C and heterogeneous catalyst of concentration 2wt%(SZ)]





[**Operating conditions**: molar ratio of alcohol: acid was 1:1, reaction temperature of 100°C and concentration of sulfated zirconia 2wt%]



Figure 13. mole fraction of oleic acid and its biodiesel.

[Operating conditions: molar ratio of alcohol: acid of 1:1,
reaction Temperature of 130°C and concentration
of sulfated zirconia 0.5wt%]

Parameter	Value
Surface area (m^2/g)	125.23
Pore volume (cm^3/g)	0.063
Bulk density (g/ml)	1.994
SO_4	8.3%
S/SZ	2.77%

Table 1. Textural properties of modified sulfated zirconia.

Fuel properties	Biodiesel Lotero, et al., 2005	Diesel Lotero, et al., 2005	Present work
Flash point °C	100-170	60–80	106
Kinematic viscosity (mm/s) @40°C	1.9–6.0	1.3–4.1	6.2289
Specific Density @60/60	0.88	0.85	0.87
Pour point °C	-15 to 10	-35 to -15	-14
Cloud point °C	-3 to 12	-15 to 5	-11
Boiling point °C	182-338	188-343	274
Carbon residue			0.013

Table 2. Biodiesel vs.	Petroleum	diesel.
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