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Simultaneous Conversion of Triglyceride/Free Fatty Acid Mixtures into Biodiesel using Sulfated Zirconia

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Abstract

Simultaneous transesterification and esterification of rapeseed oil with methanol in the presence of myristic acid was investigated. The effect of reaction temperature (120°C, 150°C and 170°C) and the effect of initial free fatty acid content in oil (0%wt, 10%wt and 20%wt) on reaction rate were studied. The catalysts were found to increase the rate of all reactions. Sulfated zirconia prepared by a solvent-free method exhibited higher activity in simultaneous reaction than the conventional method. The presence of 10% wt free fatty acids in the triglyceride increased the reaction rate and the final total fatty acid methyl esters content, and suggests that a “non-catalytic” reaction may be feasible.

Keywords: Transesterification; Esterification; Sulfated zirconia; Biodiesel; Rapeseed oil

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1 Introduction

Our main fossil fuel energy reserves are continuously decreasing, and it is predicted that they will soon fail to meet demand [1]. There are numerous attempts worldwide to develop alternative fuels from renewable sources. One such alternative fuel is biodiesel, the production of which involves the transesterification of triglycerides, usually in the form of vegetable oils, with alcohol (usually methanol) in the presence of liquid alkaline catalysts to form the alkyl ester (the biodiesel) and the major by-product glycerol (10 – 15 vol %). Other than its renewability, biodiesel's advantages include low emissions of CO, SO_x, NO_x, particulate matter and volatile organic compound (VOCs) compared to commercial diesel fuel [2]. It is also biodegradable and non-toxic.

It has been reported that the high cost of virgin vegetable oils is one of the main factors affecting the cost of biodiesel [3]. Therefore, the use of lower grade feedstocks such as non-edible oil, waste cooking oil, “yellow grease” and inedible animal fats should improve

the economic viability of biodiesel production [4]. Normally, these low-cost oils have free fatty acid contents over 2% [3]. Therefore, the application of homogeneous alkali catalysts in transesterification of such oils causes formation of undesirable products, principally soap, which is difficult to separate from the product. Acid catalysis, on the other hand, is suitable for oils with high free fatty acid content. It has the potential to catalyse both the transesterification of triglyceride and esterification of free fatty acid simultaneously without the formation of soap. This is little done in practice, as the transesterification reaction is slow when acid-catalysed, and the use of sulfuric acid increases plant capital cost due to increased cost of reaction vessels. Where high FFA feedstocks are used at all, manufacturers generally prefer to remove the FFAs by reaction with NaOH or to convert them to biodiesel via a 2-step process (acid and then alkali-catalysed) [5].

However, solid acid catalysts are preferable to liquid acid catalysts due to their easy separation from the reaction mixture, reusability and reduced waste [6]. It is well known that sulfated zirconia exhibits catalytic activity in many reactions such as esterification, etherification, alkylation, etc. as its acid strength is higher than other solid acid catalysts and homogeneous acid catalysts. Sulfated zirconia has a Hammett acid strength of $H_0 = -16$, while other solid acid catalysts such as $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ exhibit strengths below 14, and 100% sulfuric acid presents $H_0 = -11.99$ [7]. Several reports mention the application of sulfated zirconia for transesterification and esterification. Kiss *et al.* [8] reported the esterification of dodecanoic acid with 2-ethylhexanol using various solid acids such as zeolites, ion-exchange resins and mixed metal oxide, at 130-180°C. They found that sulfated zirconia was the most effective catalyst of those evaluated. Jitputti *et al.* [9] investigated the transesterification of crude palm kernel oil and crude coconut oil with methanol using several solid acids and solid basics at high temperature (200 °C). Sulfated zirconia was found to have the highest catalytic activity, with fatty acid methyl ester content higher than 90%. There are few publications on both transesterification and esterification in presence of sulfated zirconia. Garcia *et al.* [10] studied simultaneous transesterification and esterification of soybean oil in presence of 20% oleic acid with methanol and ethanol by sulfated zirconia. They identified the optimum conditions as 5% wt of sulfated zirconia, 1:20 molar ratio of oil to methanol at 120°C and 1 h, which resulted in a fatty acid methyl ester yield of 98.6%.

In this work, the simultaneous transesterification of rapeseed oil and esterification of myristic acid with methanol catalysed by sulfated zirconia at “high” temperatures were investigated. The reaction rate of both transesterification and esterification were monitored. In addition, the effect of catalyst preparation, reaction temperature and free fatty acid content were studied. Finally, the catalysts' reusability was assessed.

2 Experimental

2.1 Materials

Refined rapeseed oil was purchased from Henry Colbeck Ltd, England. The water content and free fatty acid content of this oil were determined to be 0.01 wt. % and 0.3 wt. %, respectively. Myristic acid (purity $\geq 98\%$) and silver nitrate (purity $\geq 99.5\%$) were supplied from Fluka. Zirconium (IV) oxide chloride octahydrate (purity $\geq 99.5\%$), ammonium sulfate (purity $\geq 99\%$) and Karl – Fischer reagent were obtained from Riedel de Haen. Sulfuric acid (purity $\geq 97.5\%$) and heptane for HPLC analysis were purchased from Sigma – Aldrich. Methanol (HPLC grade), 2- propanol (purity 99.99%), 35% ammonia solution (laboratory reagent grade) were obtained from Fisher Scientific. Barium chloride dehydrate was supplied from Acros Organics. Methyl heptadecanoate (purity $\geq 99.5\%$) for GC analysis from Fluka was used as an internal standard. Supelco standard 37 Component FAME mix from Sigma – Aldrich was used to identify fatty acid methyl ester peaks.

2.2 Preparation of sulfated zirconia by the solvent-free method, SF [11]

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ in a molar ratio of 1:6 were ground in an agate mortar for 20 min at room temperature (25°C). After standing for 18 h at room temperature in air, the sample was calcined at 600°C for 5 h.

2.3 Preparation of sulfated zirconia by the conventional method, CV [12]

Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) (20g) was dissolved in water (200 ml), followed by precipitation of zirconium hydroxide at $\text{pH}=9$ using a 25% w/w NH_3 solution under constant stirring in a 1000 ml beaker. After complete precipitation, it was stirred for 30 min. A white precipitate of zirconium hydroxide was washed with water to remove the chloride salts (Cl^- ions were determined with 0.5 N AgNO_3) and filtered through a Buchner funnel. In the second step, the zirconium hydroxide was dried for 24 h at 100°C , impregnated with 1 M H_2SO_4 (15 ml H_2SO_4 per 1 g $\text{Zr}(\text{OH})_4$) under constant stirring for 30 min. After filtering, the $\text{SO}_4^{2-}/\text{ZrO}_2$ was dried for 24 h at 100°C and then calcined in air at 650°C for 3 h.

2.4 Equipment

A 100 mL mini bench top reactor, model 4560 (Parr Instrument Company, Illinois, USA) was used for transesterification and esterification of rapeseed oil in presence of myristic acid. The reactor vessel was constructed from 316 stainless steel. The reactor was equipped with a magnetic stirrer drive, a four-blade impeller and thermocouple. The head assembly of the reactor was equipped with a gas inlet valve for charging N_2 gas into the reactor and a gas release valve for releasing pressure. A HPLC pump K-120 was provided for injection of material into the reactor vessel with flow rate 10 ml/min. The pressure in the reactor was used to force out the liquid samples through a dip tube which was fitted with a fine filter through the sampling tube. The process conditions including the heating mantle, reaction temperature, pressure, feed rate, and impeller speed were controlled by WinISO software from H.E.L (H.E.L Inc., Lawrenceville, NJ). The flow chart for the experimental set-up is presented in Fig. 1.

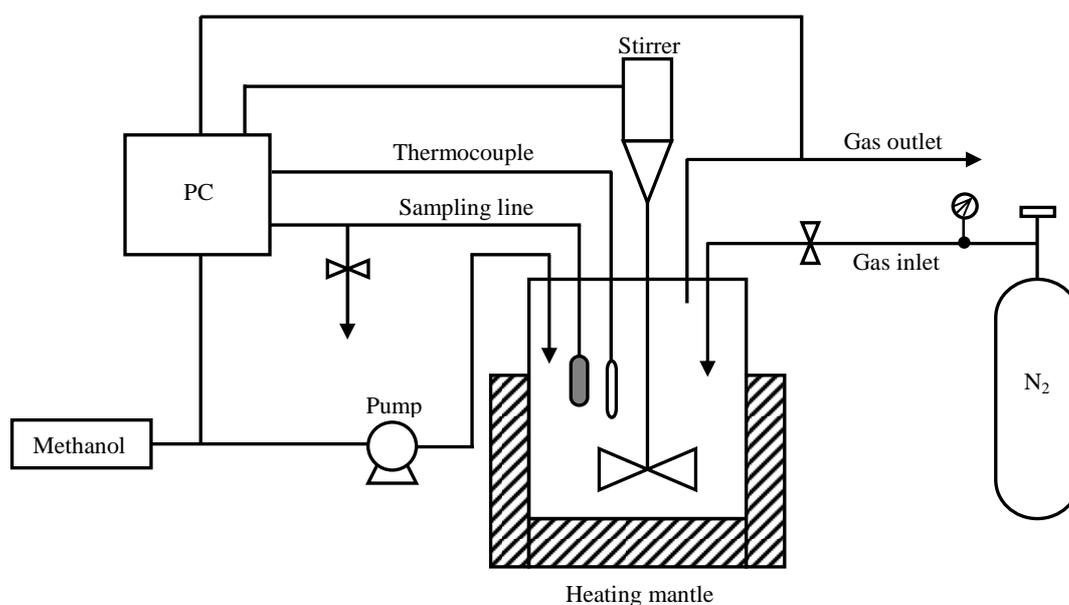


Fig. 1 Flow chart for the experimental set-up

2.5 Transesterification and esterification of rapeseed oil in presence of myristic acid

Refined rapeseed oil was used as the raw material. A typical rapeseed oil's fatty acid profile is as follows: 64.4% oleic acid, 22.3% linoleic acid, 8.23% linolenic acid, 3.49% palmitic acid and 0.85% stearic acid [13]. Initially, 30 g of the oil with myristic acid and catalyst were charged to the reactor. In order to prepare oil samples with various percentages of myristic acid accurately, a calibration curve relating the concentration of myristic acid in

oil to the weight of myristic acid used was performed using a titration with 0.025 N NaOH. The slope of the correlation was 2.708 with R² of 0.99. After the reactor was closed, nitrogen was used in order to purge the air left in the reactor. When the reactant and catalyst reached the desired reaction temperature, with stirring rate at 600 rpm, nitrogen was introduced to pressurise the system to ensure that at the desired reaction temperature the reactants are in the liquid phase. The reaction was started when methanol was added into the reactor. Liquid samples were withdrawn through a sampling line throughout each run.

2.6 Leaching and reusability of catalyst

Catalyst reusability and leaching were investigated by filtration of the reaction product to separate solid catalyst. After drying at 100 °C for 24 h, the catalyst was divided to study its reusability. Approximately 300 mg of the remaining catalyst were stirred with 50 mL distilled water for 3 h. The suspensions were then filtrated and the acidity was measured by titration with KOH 0.002N. BaCl₂ solution was also used to identify sulfate ion from the leaching of catalyst. Fresh catalyst was also treated following the same procedure.

2.7 Analytical methods

The withdrawn samples were allowed to settle overnight to separate into two layers. The fatty acid methyl esters in the oil phase were analyzed by a Hewlett Packard 5890 Series II gas chromatograph (GC) equipped with flame ionization detector (FID) and a fused silica capillary column (30 m x 0.32 mm x 0.25 μm). The GC oven temperature was 210 °C using helium as a carrier gas, the FID was maintained at 250°C and injector temperature at 250°C. A 10 mg/mL of methyl heptadecanoate solution was used as the internal standard and the fatty acid methyl esters content were calculated by comparing the peak area between the sample and methyl heptadecanoate. The peak identification was made by comparing the retention time between the sample and the standard compound. In addition, the oil phase free fatty acids content was determined by titration of the sample in 2-propanol with 0.025 N sodium hydroxide using phenolphthalein as indicator. The amount of water in both the oil and aqueous phases was measured using the Karl-Fischer titration (Metrohm, model 701 Titrino).

3 Results and Discussion

3.1 Catalysed and Noncatalysed Reaction

The catalysed simultaneous transesterification and esterification reaction of rapeseed oil with 10 % myristic acid (CTE) using sulfated zirconia prepared by the “solvent-free method” was studied. The reaction parameter included oil/methanol molar ratio 1:20, 3% catalyst at 170°C. In addition, the catalysed transesterification of rapeseed oil (CT) and the catalysed pure esterification reaction of myristic acid (CE) were investigated at the same conditions. Non-catalysed simultaneous transesterification and esterification of rapeseed oil with 10%wt myristic acid (NTE), the non-catalysed pure transesterification reaction of rapeseed oil (NT) and the non-catalysed pure esterification reaction of myristic acid (NE) were used to compare the reaction rate. The reaction profiles are presented below, in Fig. 2.

NB: In the following graphs (Figs 3 & 4) the nomenclature used is:
 C: catalysed, N: non-catalysed, TE: combined transesterification and esterification, T: transesterification only, E: esterification only.

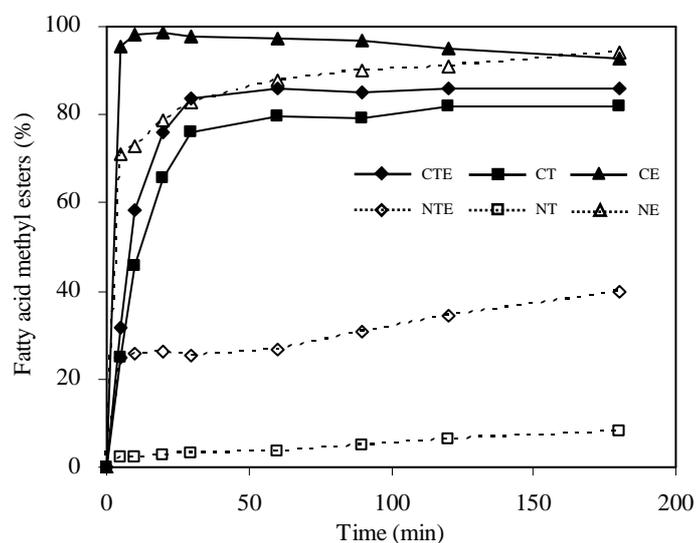
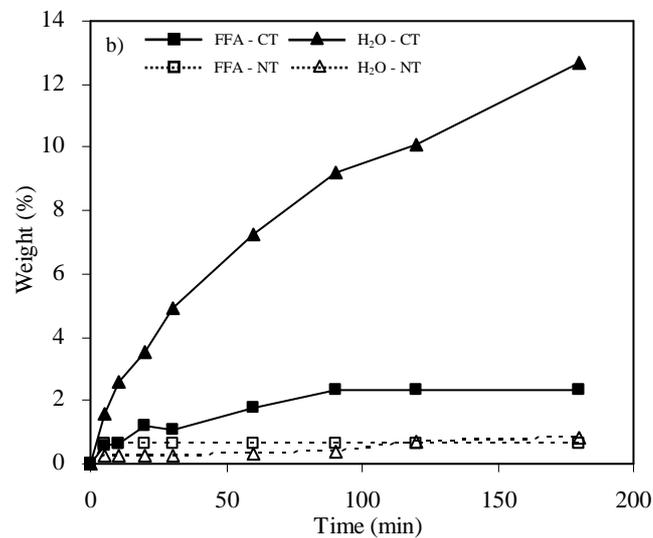
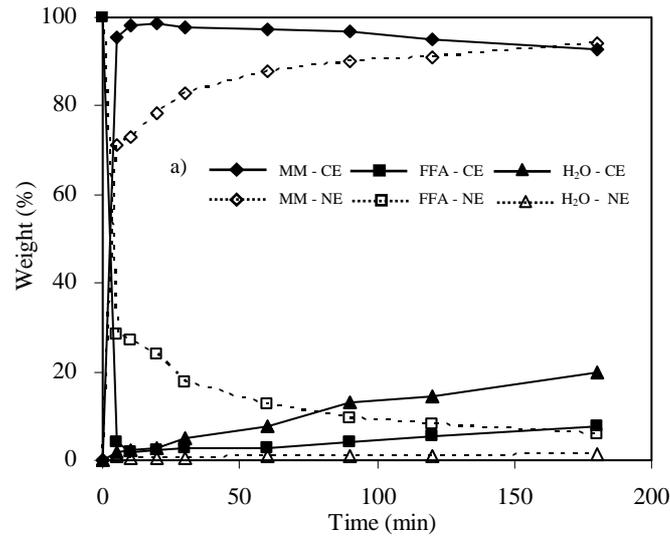


Fig. 2 Comparison of fatty acid methyl esters content of the catalysed reaction using 3%wt catalyst prepared by solvent-free method and non-catalysed reaction, 1:20 molar ratio of oil to methanol, stirring rate 600 rpm, reaction temperature 170°C.

It is clear that the presence of sulfated zirconia increased the rate of transesterification: the reaction rates exhibited in the CTE and CT experiments were much higher than their non-catalysed analogues (NTE and NT, respectively). In addition, the presence of myristic acid in both catalysed and non-catalysed reactions also increased the overall reaction rate. This is particularly evident in the FAME concentrations observed at the end of the experiment: 8% in the non-catalysed triglyceride-only experiment and 40% in the non-catalysed experiment. Also, despite the initial reaction rates of CE and NE being fairly similar, the fatty acid methyl ester contents achieved after 10 minutes were 98% and 73%

respectively, although they do cross later on, as the FAME concentration decreases after ~20 minutes in the catalysed fatty acid-only experiment. This can be correlated with increasing free fatty acid and water content (Fig. 3a, following, MM is myristic acid methyl ester). These trends are not observed in the “NE” reactions, where the myristic acid methyl ester simply follows the loss of the acid.



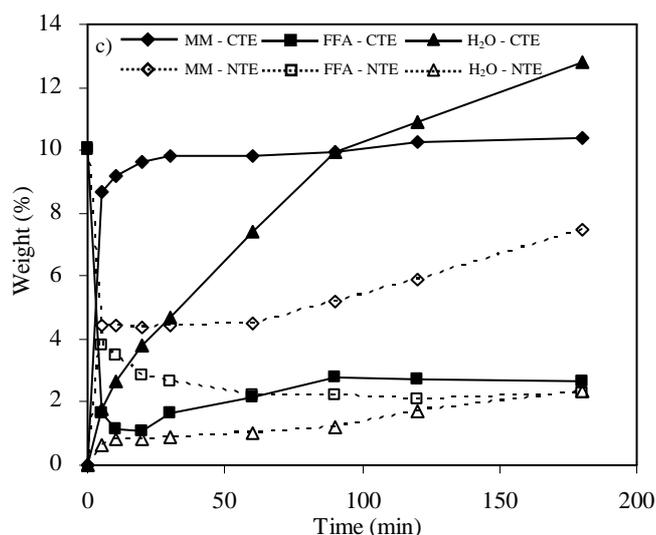


Fig. 3 Changes in weight percentage of myristic acid methyl ester, free fatty acids and water content in a) the catalysed and the non catalysed esterification of myristic acid b) the catalysed and the non catalysed transesterification of rapeseed oil c) the catalysed and the non catalysed simultaneous transesterification and esterification reaction.

Clearly the ester and water accumulates in the reaction mixture with the catalyst promoting the reverse reaction to form free fatty acids. Even though the hydrolysis of ester (the “CE” reaction) and/or the reaction was complete, the water concentration continued to increase. This might be due to dehydration of excess methanol, but this is unproven as yet and is the subject of further study. All these reactions are represented in Fig. 4 below.

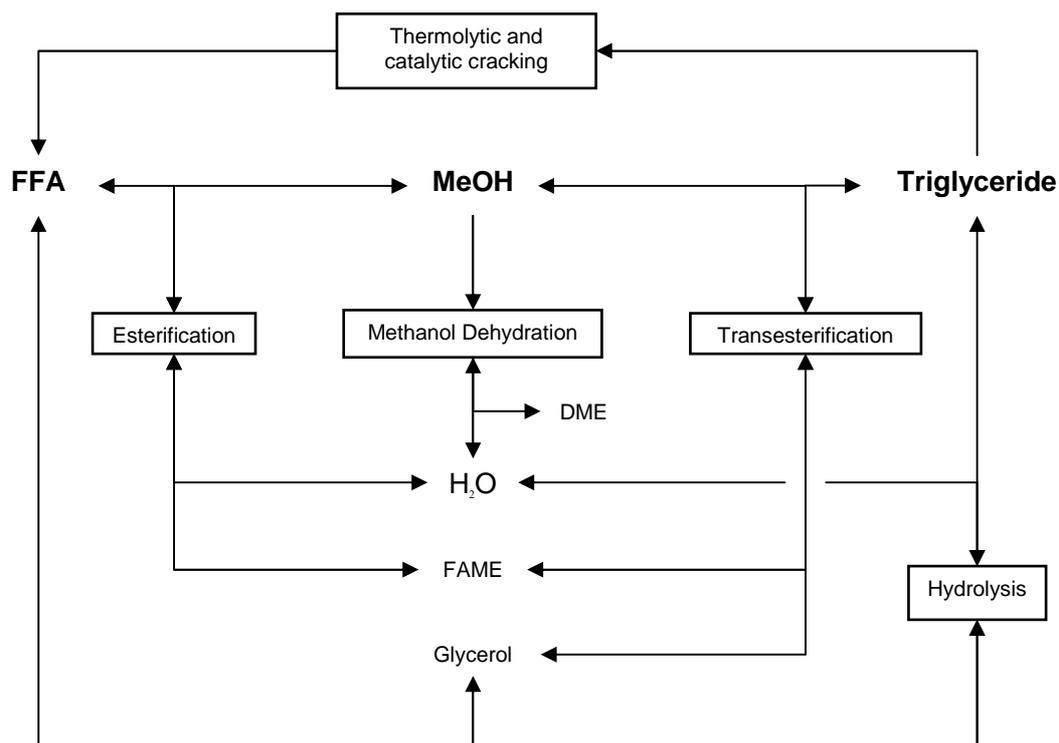


Fig. 4 Reaction Pathways in combined esterification/transesterification systems.
Initial reactants marked in bold.

In Figure 4 note that (i) no distinction is made here between rapeseed-derived methyl esters and myristic acid-derived (to keep the diagram relatively) simple (ii) most of the reactions are significantly reversible (as indicated by the double-headed arrows), but have been give the name of the “forward” reaction where possible (iii) monoglyceride and diglycerides have been left out for the sake of simplicity (the 3 step transesterification to glycerol is shown as 1 step) (iv) numerous other products of the cracking reactions are possible but are not shown here.

The FFA content after 20 min was observed to increase in CTE and CT (Fig. 3b, 3c). To confirm that the free fatty acids content obtained in oil phase of reaction mixture was not contaminated with free acids obtained from the leaching of catalyst, the oil phase was stirred in distilled water for 24 h and the filtrate tested with BaCl₂ solution. No free acids were found in the oil phase. There was no matching decrease in myristic acid methyl ester, so hydrolysis of methyl myristate can be neglected. However, total fatty acid methyl ester did increase to get the complete conversion therefore hydrolysis of ester may appear at final reaction time. Side-reactions such as thermolytic and catalytic cracking of the triglyceride may cause the accumulation of free fatty acid [2]. Moreover, the water that accumulated in the reaction mixture would lead to hydrolysis of triglyceride to form free fatty acids. The formation of water during CT was observed as it was in CTE. In addition, no glycerol layer was observed

during both reactions as might be expected some free glycerol might be contaminated in upper aqueous layer. The explanation may be that FAME was produced through thermolytic/thermocatalytic reaction coupling on esterification of free fatty acid more than that transesterification as led to the generation of water. Moreover, dehydration of excess methanol is another source of water.

3.2 Effect of catalyst preparation on reaction rate

There are two sulfated zirconia preparations commonly mentioned in the literature. Sulfated zirconia prepared by the “conventional method” (here referred to as “CV”) was developed by Yadav and Nair [12]. The preparation method involves the calcination of a $Zr(OH)_4$ precursor impregnated with sulfating agent at 550-650°C. The CV catalyst prepared by using 1M H_2SO_4 and 650°C of calcination temperature gave the best properties (Table 1). Sun *et al.* [11] presented sulfated zirconia preparation by a “solvent-free method” (“SF”). The method involves calcination of $ZrOCl_2 \cdot 8H_2O$ mixed with $(NH_4)_2SO_4$ at 600°C in the absence of any solvent. The molar ratio of $ZrO_2 \cdot 8H_2O$ to $(NH_4)_2SO_4$ generally between 1:6 and 1:10 has been studied. The BET surface area increased with an increase of $(NH_4)_2SO_4$ content as shown in Table 1. However, the optimum ratio of 1:6 was used to test in various reactions.

In this work, the effect of both catalysts on the reaction rate of the simultaneous reaction was studied. The results are given in Fig. 5, below.

Catalysts	BET surface area (m^2/g^{-1})	Sulfate content (%)	Pore volume (cm^3/g)	References
SF (1:6 $ZrO_2 \cdot 8H_2O/$ $(NH_4)_2SO_4$)	165.1	7.7	0.34	[11]
SF (1:6 $ZrO_2 \cdot 8H_2O/$ $(NH_4)_2SO_4$)	126	-	-	[10]
SF (1:10 $ZrO_2 \cdot 8H_2O/$ $(NH_4)_2SO_4$)	193	-	-	[11]
CV (1 M H_2SO_4 , at 650°C)	100	-	0.11	[12]
CV (1 M H_2SO_4 , at 650°C)	118	2.5	0.10	[8]
CV (0.5 M $(NH_4)_2SO_4$), at 600°C)	86.8	4.3	0.10	[11]
CV (0.5 M H_2SO_4 , at 650°C)	89	-	-	[10]

Table 1 Comparison of the catalyst properties between SF and CV method

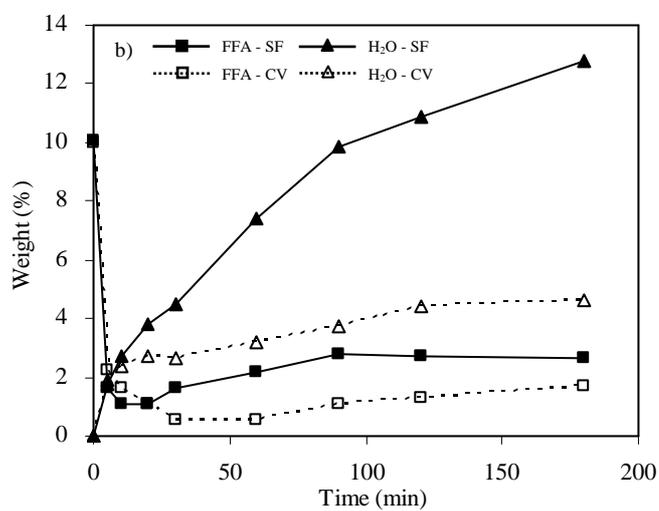
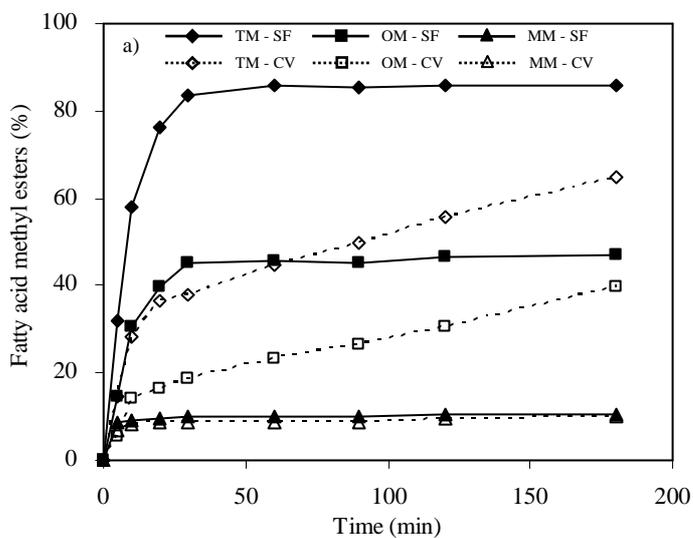
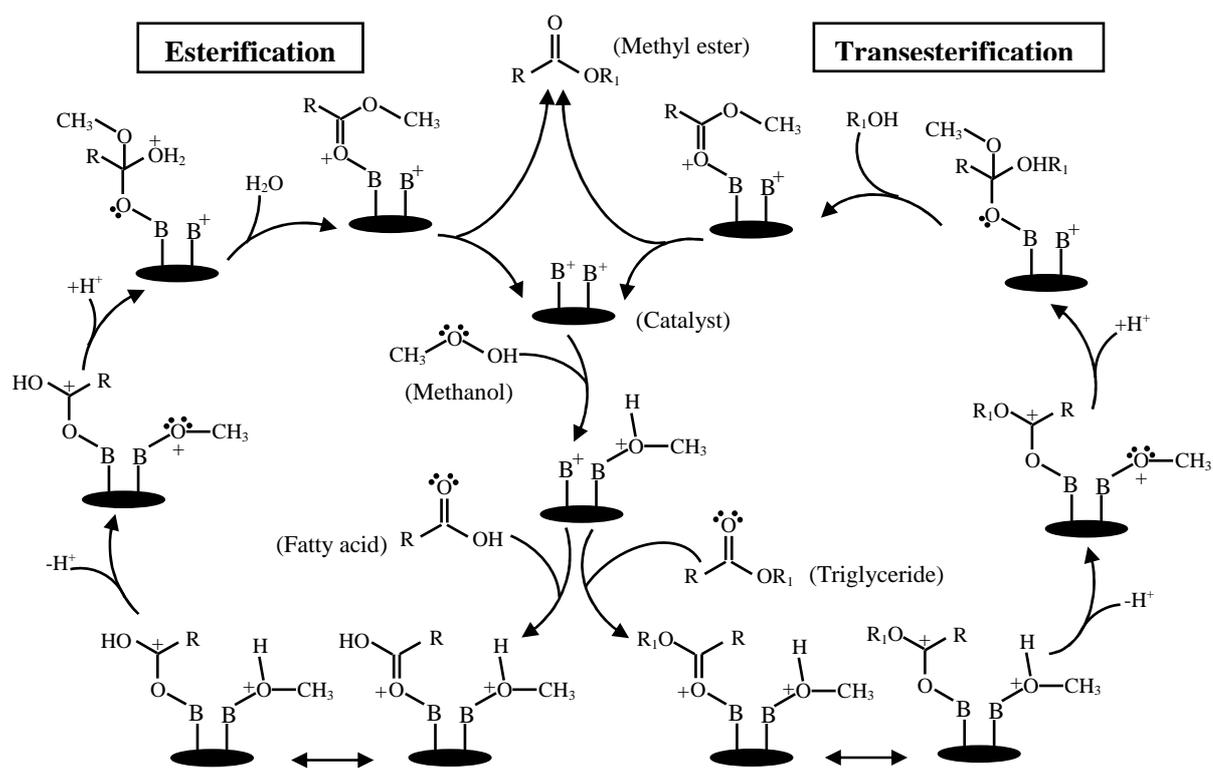


Fig. 5 Effect of catalyst preparation on reaction rate of simultaneous transesterification and esterification in presence of 10%wt myristic acid using 3%wt catalyst, 1:20 molar ratio of oil to methanol, stirring rate 600 rpm, reaction temperature 170°C.

The SF catalyst demonstrated a higher activity in simultaneous reaction than the CV catalyst. The highest level of total fatty acid methyl esters (TM) obtained from the SF reaction was 85% after 1 h at 170°C whereas use of the CV catalyst resulted in total fatty acid methyl ester of only 45% after 1 h at the same condition. The oleic acid methyl ester (OM) and myristic acid methyl ester (MM) were used to monitor the reaction rate of transesterification and esterification respectively. The reaction rate of both the transesterification and esterification were higher when using SF catalyst than CV catalyst. A number of reports have suggested that the dependency factors included surface area, tetragonal phase of ZrO₂ and acidic site. Sun *et al.* [11] and Garcia *et al.* [10] reported that the higher BET surface area of SF catalyst compared to CV catalyst that the larger surface area caused the higher catalytic activity. It has been reported that SF catalysts exhibit broad band peaks in XRD, indicating that smaller zirconia particles are formed [11]. Generally, sulfated zirconia exhibits both Bronsted and Lewis acid sites. However, whether the strong active sites in this catalyst result from Bronsted, Lewis or combinations of both acid sites is still unclear [12]. Li *et al.* [14] found more Lewis acid sites than Bronsted in CV catalysts. Sun *et al.* [11] reported that SF catalysts have many more Bronsted acid sites than CV catalysts, and this may explain their higher catalytic activity in esterification and cracking. Therefore, it is possible that triglycerides/free fatty acids during simultaneous transesterification and esterification are preferentially adsorbed on the Bronsted acid sites of sulfated zirconia. The reaction is probably following Langmuir-Hinshelwood mechanism (scheme 1). The hydroxyl group of methanol is protonated by Bronsted acid on the catalyst surface while the protonation of fatty acid/triglyceride on an adjacent site leads to the carbocation. Deprotonation of methanol oxygen produces the nucleophile, which attacks the carbocation to generate a tetrahedral intermediate. The tetrahedral intermediate eliminates water to form ester. In transesterification, this intermediate eliminates glycerol to generate a new ester. This mechanism can be extended to di- and tri-glycerides.



B^+ = Bronsted acid site on the catalyst surface

R = alkyl group of fatty acid

R_1 = alkyl esters of triglyceride

Scheme 1

FFAs increased after 20 min when using the CV catalyst but this was significantly less than when using the SF catalyst, and there was no resultant decrease in myristic acid methyl ester content. In addition, the water accumulated in reaction mixture in SF catalyst was also more than in CV catalyst. Therefore, it is further evidence that the catalytic mechanism is linked to free fatty acid and water content.

3.3 Effect of reaction temperature on reaction rate

Reaction temperature would be expected to influence the reaction rates of both transesterification and esterification. To determine the effect of this parameter, simultaneous transesterification and esterification of rapeseed oil with 10% myristic acid was performed at temperatures in the range 120 - 170°C. Conversion-time data are represented in Fig. 6, below. The reaction rate of oleic acid methyl ester, which represented the transesterification rate, increased with the increasing reaction temperature. However, myristic acid methyl ester, the marker for esterification, exhibited very rapid reaction rates at all reaction temperature, being essentially complete after 20 minutes. It is possible that transesterification using heterogeneous catalyst requires high temperatures to overcome mass transfer and solubility

limitations. An increase in free fatty acid content after 20 min at reaction temperature 170°C was observed, while at 150°C and 120°C this was observed after 30 min. The water content was observed to increase with reaction temperature.

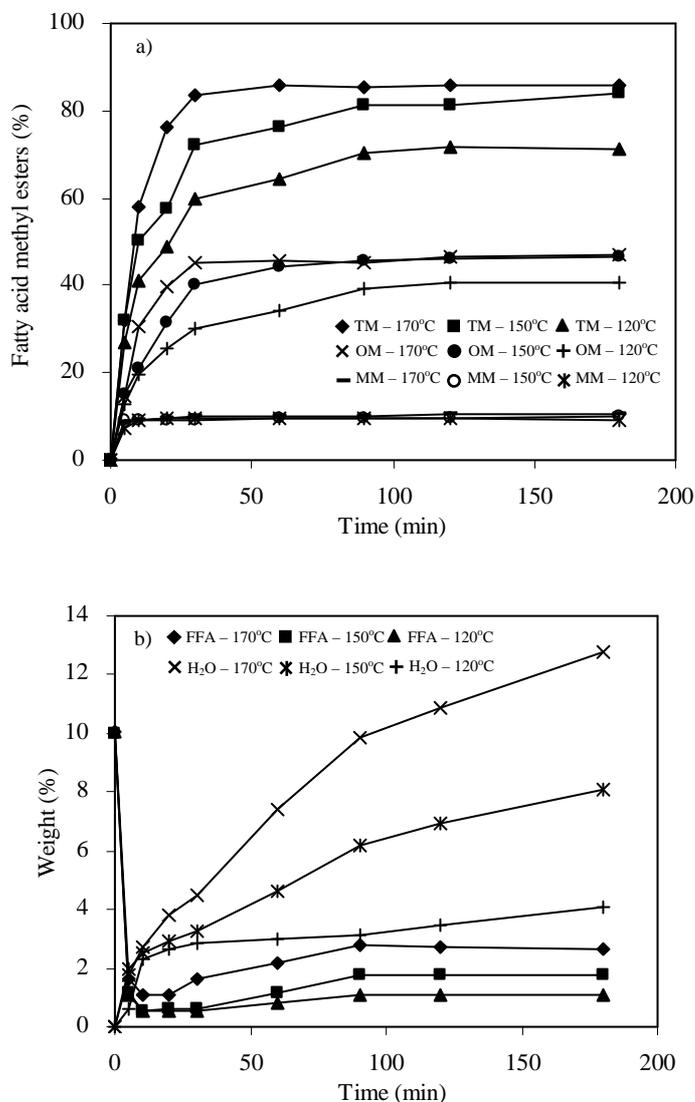


Fig. 6 Effect of reaction temperature on reaction rate of simultaneous transesterification and esterification in presence of 10%wt myristic acid using 3%wt sulfated zirconia prepared by solvent-free method, 1:20 molar ratio of oil to methanol, stirring rate 600 rpm.

3.4 Effect of myristic acid content in oil on reaction rate

High free fatty acid content may affect reaction rates or final ester contents. To investigate the effect of this parameter, reactions with 0% wt, 10% wt and 20% wt myristic acid in oil were performed.

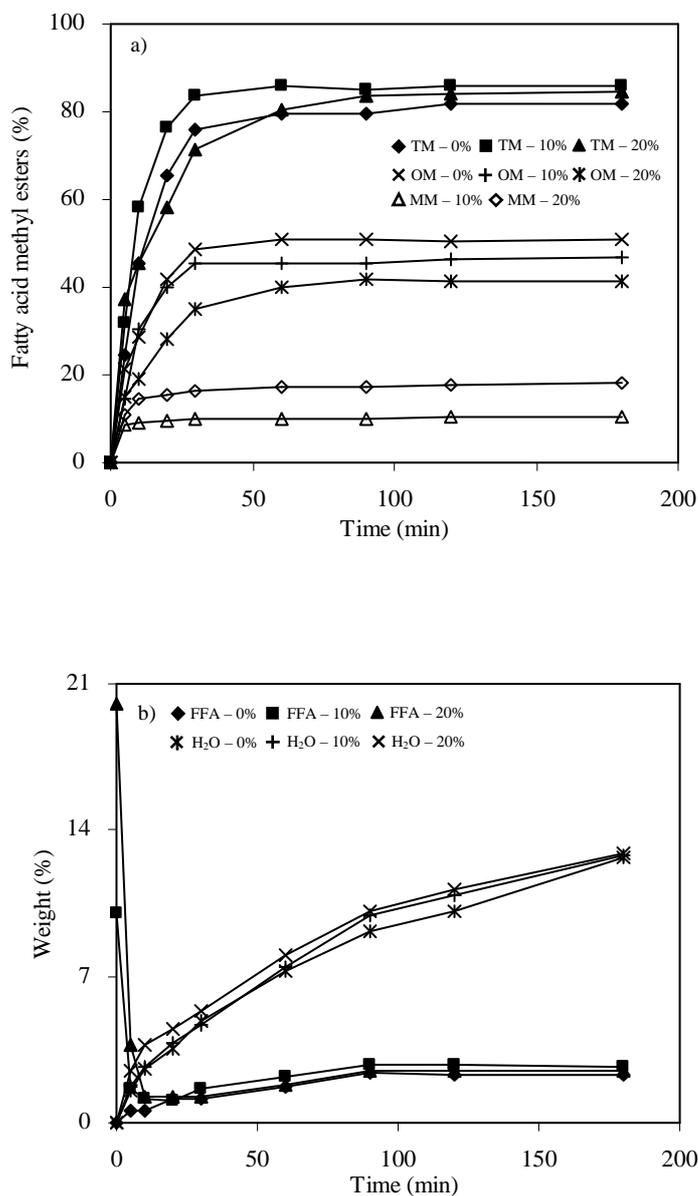


Fig. 7 Effect of myristic acid content in oil on reaction rate of simultaneous transesterification and esterification using 3%wt sulfated zirconia prepared by solvent-free method, 1:20 molar ratio of oil to methanol, stirring rate 600 rpm at 170°C.

Fig. 7 shows that the rate of oleic acid transesterification decreased with increasing myristic acid. However, the rate of formation of myristic acid methyl ester also increased with increasing amount of myristic acid. The rate of production of total fatty acid methyl esters increased when increasing the initial myristic acid from 0 wt % to 10 wt %. However, a slight decrease is observed when higher levels of myristic acid (20% wt) were used. This may be due to rapid formation of esters by esterification of myristic acid which promotes the reverse transesterification reaction of ester with glycerol, thereby slowing down the transesterification [15].

In the 0 wt % myristic acid experiment, free fatty acids content increased with time. After 20 min, when much of the initial charge of myristic acid in the other experiments had been consumed, its trajectory was essentially the same as when using 10 wt % or 20 wt % myristic acid. The water contents in all reactions were also not significantly different. This implies that most of the free fatty acid and water content in the reaction mixture were produced from reaction of rapeseed oil. There are three possible types of side-reaction which could occur at these pressures and temperatures to produce free fatty acids and water: thermolytic/thermocatalytic reaction, glycerolysis of free fatty acid and hydrolysis of triglyceride (these reactions are represented in Fig. 4).

3.5 Leaching and reusability of catalysts

Table 2 Acidity (measured by titration with 0.002 N KOH) for fresh catalyst, spent catalyst and reaction layers

SF catalyst type /reaction layer	Free acid concentration (M)
Fresh catalyst	8×10^{-3}
Spent catalyst 120°C	4.1×10^{-3}
Spent catalyst 150°C	3.5×10^{-3}
Spent catalyst 170°C	1.2×10^{-3}
Upper reaction layer 120°C	2.4×10^{-2}
Upper reaction layer 150°C	2.4×10^{-2}
Upper reaction layer 170°C	2.2×10^{-2}
Lower reaction layer 120°C	-
Lower reaction layer 150°C	-
Lower reaction layer 170°C	-

It is well known that sulfated zirconia is a solid catalyst of high acid strength. However, the leaching of sulfated groups is a limitation to their use in reactions involving water. The water can capture sulfated groups from surface and hydrolyze them to give homogeneous H_2SO_4 [8]. Spent catalysts prepared by the solvent-free method in reaction mixtures at temperature 170°C, 150°C and 120°C were tested the leaching of sulfate group into the reaction mixture, while fresh catalyst was used to compare. After stirring the catalyst with water for 3 h, the hydrolysis of the sulfate group was measured by titrating the filtrate against 0.002 KOH (Table 2). The fresh catalyst was demonstrated to leach by hydrolysis. Sulfate group hydrolysis increased with decreasing reaction temperature. The concentration of

free acid (H^+) leached into the reaction mixture at various reaction temperatures was also determined. The lower phases, as they were organic, were extracted by water for 24 h and then the acidity of the filtrates were measured. No free acid was found in this phase at any reaction temperatures. Even though the water content in the reaction mixture increased with increase reaction temperature, free acid content in upper phase (aqueous phases) exhibited no significant increase with increasing reaction temperature (Table 2). Covering the surface with organic hydrophobic components, such as triglyceride, intermediate glycerides and free fatty acids on surface of catalyst is thought to protect acidic sites from hydrolysis [16]. Higher temperatures would affect the mass transfer of these components. The presence of sulfate ions in water was also confirmed by $BaCl_2$ test. A white precipitate in water was obtained from stirring spent catalyst. This demonstrates that the sulfate ion did leach into the reaction mixture.

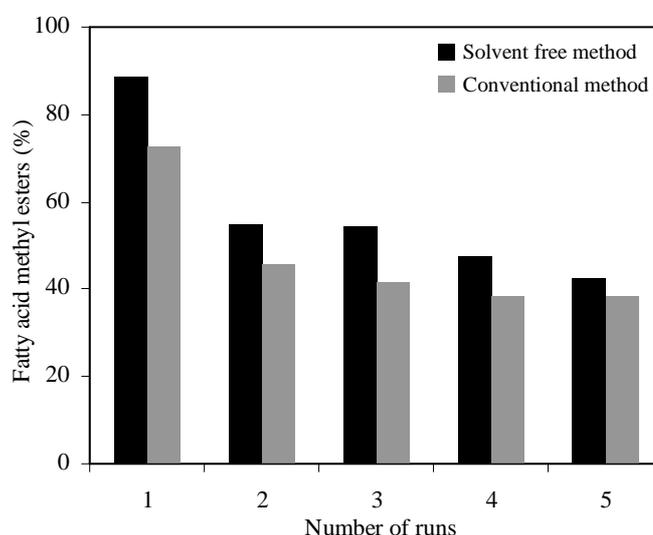


Fig. 8 Reusability of catalyst in simultaneous transesterification and esterification reaction of rapeseed oil using 3%wt catalyst, 1:20 oil: methanol molar ratio, stirring rate 600 rpm at 170°C for 3 h.

The reusability of the catalyst was assessed. In order to study the catalyst reusability, both sulfated zirconia prepared by the solvent-free method and convention method were filtered from the reaction mixture and then dried at 100°C for 24 h. Simultaneous transesterification and esterification of rapeseed oil with 10% wt myristic acid was carried out using 3% wt of fresh and spent catalyst, 1:20 molar ratio of oil to methanol at 170°C. The catalysts prepared by both methods exhibited significant catalytic activity loss on the second run, and thereafter a slower gradual loss. For the solvent-free method fatty acid methyl esters content in second run, third run, fourth run and fifth run were 55%, 54%, 47% and 42%

respectively. This implied that the main route of catalyst deactivation occurs by sulfate ion leaching.

Table 3 is a comparison of catalyst performance in simultaneous transesterification and esterification by different heterogeneous catalysts. It can be noted that sulfated zirconia prepared by solvent-free method (SF) is a promising heterogeneous catalyst for biodiesel synthesis from low grade and/or waste oils. If this were to be an industrially useful catalyst it would have to overcome its limitations due to leaching.

Table 3 Comparison of catalyst performance in simultaneous transesterification and esterification by different heterogeneous catalyst

Catalyst	Initial FFA conc. (% wt)	Reaction temp. (°C)	Catalyst loading (% wt)	Molar ratio oil/ alcohol	Reaction time (h)	Ester yield (%)	Reference
TPA/HZ ^a	20	200	3	1:9	10	90	[17]
Zn/Si ^b	15	200	3	1:18	10	98	[18]
Zn ₃ La ₁	5.4	200	2.3	1:36	3	96	[19]
SO ₄ ²⁻ /TiO ₂ -SiO ₂	50	200	3	1:9	6	92	[20]
Mg-Al-CO ₃ hydrotalcite	43	200	1	1:6	3	99 ^c	[21]
SO ₄ ²⁻ /ZrO ₂ by SF method	10	170	3	1:20	1	86 ^c	This experiment

^a12-Tungstophosphoric acid supported on hydrous zirconia

^bZinc stearate immobilized on silica gel

^cConversion (%)

4 Conclusion

Sulfated zirconia, prepared by two different methods (the solvent-free method and the “conventional” wet impregnation method) was found to be an efficient catalyst for simultaneous transesterification and esterification of rapeseed oil in the presence of 10 wt % myristic acid. Use of sulfated zirconia produced by the solvent-free method was demonstrated to result in substantially higher rates of both transesterification and esterification. However, the reusability of both forms is questionable as their activities fall significantly on second use, (although subsequent reuse results in more modest reductions). Leaching of sulfate ions is likely to be the main route to loss of catalytic activity of sulfated zirconia in these reactions. It remains to be seen whether this lower level of activity is maintained over many cycles of reuse and, if so, whether it could be enough to be the basis of an economically viable process. Other avenues for overcoming this problem include catalyst modification to increase stability,

or catalyst regeneration. Simple regeneration via calcination, for instance, has not been attempted in this study.

Importantly, the presence of 10 wt % free fatty acids in oil was shown to significantly increase the initial reaction rate, regardless of whether catalyst was present. This opens up the possibility of a “non-catalytic” process for fatty acid/triglyceride mixtures, where the FFA is to some extent catalysing the triglyceride’s transesterification. The reaction rate decreased when fatty acids content was increased to 20 wt %, but substantial scope for optimisation of the reaction conditions remains. Esterification, for example, was shown to be complete in a relatively short time in the temperature range used here, but the rate of transesterification was sensitive to temperature within this range. Future work will investigate this effect further to determine optimum FFA/triglyceride ratios and the catalytic effect of the vessel.

Overall, this reaction system is attractive for industrial biodiesel production as it can potentially be applied to convert inexpensive, low grade and/or waste oils, which typically have high free fatty acid contents, into saleable biodiesel.

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