



## Harnessing Alternative Technology for the Sustainability of Biodiesel Production

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### ABSTRACT

Biofuel, a renewable energy is mainly produced by transesterification of fatty acids either in presence of enzyme or catalysts. The transesterification relies on the use of either strong base or strong acid homogeneous catalysts for effective performance; but, homogeneous catalysts are associated with a variety of technical hurdles that limit their use for biodiesel production. Although there have been recent developments in heterogeneous catalysts for biodiesel production via transesterification; the separation of methyl ester (FAMES) from crude glycerol and alcohol recovery are still major hindrances. A possible alternative could be the use of solid acid catalysts in thermocatalytic cracking of triglycerides. Sulphated zirconia catalyst was evaluated for thermocatalytic cracking of triglycerides at a relatively low temperature (270°C) and atmospheric pressure. The catalyst was found to be active toward cracking vegetable oils to methyl esters. The catalyst at this temperature exhibited different selectivity towards formation of saturated and unsaturated methyl esters. The catalyst yield of methyl esters under these conditions was 58% while 80% of the product being unsaturated. This opens up the possibility of controlling the degree of saturation of the methyl ester product by catalyst choice, to produce more or less saturated fuels for different markets. The range of products from gases to middle distillates and the unique selectivity for saturated and unsaturated esters may be a significant process advantage of this form of catalytic cracking. An important long chain unsaturated alcohol (1-Heptatriacotanol) was also identified. The unsaturated alcohol is known as an industrial chemical.

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## INTRODUCTION

One of the most significant problems of the biodiesel industry is the cost of production, due to the costs of the raw material (usually vegetable oil) and the processing costs. The current method of production is via “transesterification” reaction, which usually involves reacting methanol/sodium hydroxide mix with high-quality vegetable oil in batch reactors. Although biodiesel is produced on a large scale by transesterification, there are still many problems such as: non-flexibility of feedstock, intolerance to water and the extensive separation steps required to achieve biodiesel fuel grade specifications [1]. This has kept, and is still keeping, the retail price of biodiesel too high to be competitive with fossil fuel-derived diesel (without

subsidies or legislation). In principle, thermocatalytic cracking using appropriate catalyst can reduce the numerous downstream processing steps by converting triglycerides directly to biodiesel. The detailed mechanism of thermocatalytic cracking is not well-established. However, several researchers [2, 3] reported similar pathway for catalytic cracking of triglyceride molecule. It is initiated with a thermal cracking process by means of free radicals. In the presence of a catalyst with active acid sites accessible for triglyceride molecules, the triglyceride decomposes by means of interaction of the oxygen bonding of the ester carbonyl groups with an acid site. Summarily, the reaction occurs via two steps: (i) decomposition of triglycerides to carboxylic acids, acrolein and ketenes. These compounds recombine at the reaction conditions to form esters,

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carboxylic acids and hydrocarbons as shown in Figure 1; (ii) the carboxylic acids are decarboxylated or decarboxylated, producing, respectively, carbon monoxide, olefins and water or carbon dioxide and paraffins.

The hydrocarbons undergo further chemical processes such as alkylation, isomerisation, and polymerization. The occurrence of these different reaction routes depends on the catalyst activity and double bonds in the initial oxygenated hydrocarbon, as well as the reaction conditions. Research in this area is substantially less advanced than in transesterification of oil to biodiesel [4]. The main advantage of this process compared to transesterification is that a range of gaseous products to middle distillates are produced [5]. The greatest challenge in the industry has to do with choice of catalysts with high activity to enhanced selectivity of the desired, higher value products [6] i.e. the middle distillates. In this research the focus was on methyl ester selectivity, as it is an established biofuel.

Heterogeneous catalysts have only been recently investigated for biodiesel production by catalytic cracking [7]. The main challenge is to develop a catalyst that exhibits high activity and selectivity towards the production of methyl ester. Kirszensztejn et al. [8] investigated the use of sulphate of zirconia and its modified form (with boron oxide) in cracking rapeseed oil to produce biofuel at 773–923 K and atmospheric pressure. Their liquid product was a mixture of water, aliphatic and aromatic compounds, while the gaseous product consisted of carbon dioxide and hydrogen. Among all heterogeneous solid acid catalysts, zirconium oxide doped with sulphate has attracted considerable attention due to its high acidity which makes it an effective solid acid catalyst for acid-promoted reactions [9]

In this work, non-crystalline sulphated zirconia catalyst was used for thermocatalytic cracking of triglycerides to biofuel. For comparison purposes, the same feedstock was thermally cracked under the same operating conditions. The ultimate aim of this research is to produce biofuel (biodiesel) from triglyceride using an alternative method in transesterification process.

## MATERIAL AND METHODS

The catalyst was contacted with triglycerides in a 100 ml batch reactor mixed with a magnetic stirrer. The reactor was equipped with auto sampling port and an external heating mantle. The oil was heated to 270°C before the catalyst was injected. Samples were taken at intervals of 15 minutes throughout the course of reaction time for duration of 3 hours. The fatty acid methyl esters (FAMES) content in the collected samples was determined using the BS EN 14103:2003 approach on

Hewlett Packard 5890 Series II gas chromatograph with the aid of FID detector. The column temperature was maintained at 210°C, while the FID and injector were operated at 250°C. Other products in the samples were identified on GC-MS (Perkin Elmer (Clarus) 600/560D) in accordance with BS EN 14105:2003 procedure. Calibration curves were prepared using stock solutions of glycerol, triolein, diolein and monoolein in pyridine as specified in the BS EN 14105:2003. Equations 1 and 2 were used to evaluate the concentration of total and individual ester content respectively, expressed as a mass fraction in percentage. The yield was calculated based on the feed while selectivity of saturated or unsaturated esters was based on the total methyl esters.

$$C = \frac{(\sum A) - A_{E1}}{A_{FI}} \times \frac{C_{E1} V_{E1}}{M} \times 100\% \quad (1)$$

$$L = \frac{A_L}{(\sum A) - A_{E1}} \times 100\% \quad (2)$$

where:

$\Sigma A$  is the total peak area on the chromatogram ( $C_{14}$  to  $C_{24:1}$ )

$A_{E1}$  is the peak area corresponding to methyl heptadecanoate (IS)

$C_{E1}$  is the concentration of methyl heptadecanoate (mg/ml)

$V_{E1}$  is the volume of the methyl heptadecanoate used (ml)

$A_L$  is the peak area corresponding to the individual ester of interest

$m$  is the mass of the sample (mg)

## RESULTS AND DISCUSSION

Conversion of the triglycerides is shown in Figure 1. The catalyst was active in conversion of triglyceride to products (about 75% of the feed was converted).

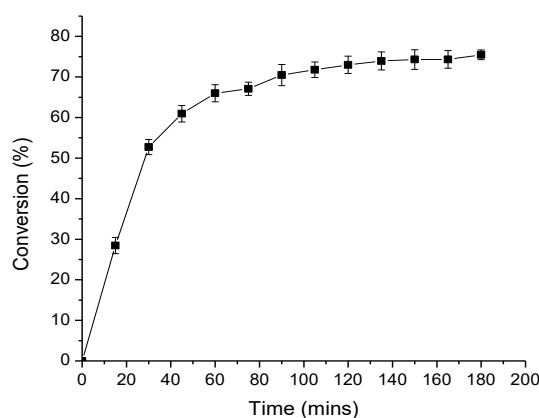


Figure 1. Conversion of triglycerides

However, the catalyst exhibited 58% yield for methyl

ester as shown in Figure 2. This is relatively high compared to earlier reports [10],[11]. This is clearly attributed to the active sites on the catalyst used. A reduction in the methyl ester after a reaction time above 2h was observed. This could be due to further breakdown of the methyl ester into other forms of biodiesel [12]

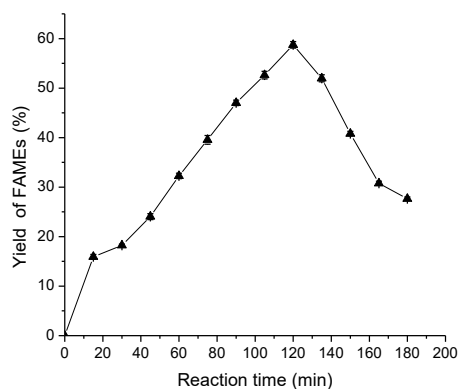


Figure 2: Methyl esters yield with respect to catalyst

The product distributions revealed the presence of free fatty acid, diglycerides in addition to methyl esters in the liquid product mixture. The product profile showed the cracking of triglycerides into free fatty acid which was further cracked and recombine to form the different products; data are illustrated in Figure 3. The percentage of free fatty acid in the product mixture is an indication of the ability/activity of the catalyst to further breakdown the free fatty acid which is the first primary product during cracking. The gases identified were carbon monoxide, methane, propane, hydrogen and water. However, they were not quantified.

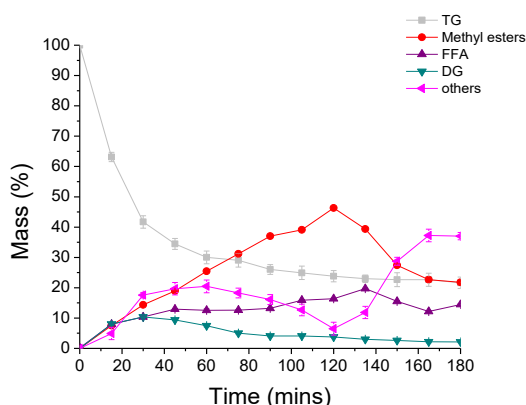


Figure 3: Product Distributions

Interestingly, the catalysts were not just active for fatty acid methyl ester but in addition exhibited some selectivity for saturated and unsaturated methyl esters; results are shown in Figure 4. The conventionally prepared crystalline sulphated zirconia catalyst was earlier reported as more selective to saturated methyl

esters [13]. However, the present non-crystalline sulphated zirconia catalyst was more selective for unsaturated methyl esters.

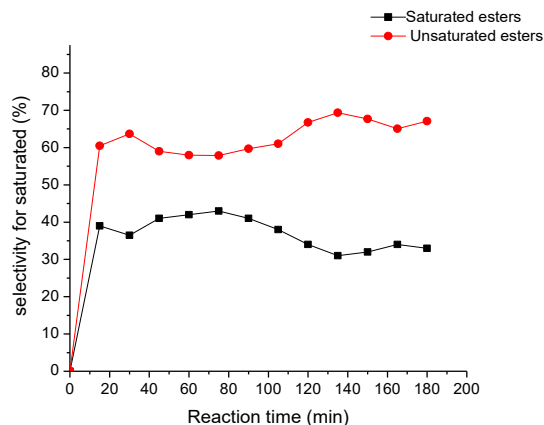


Figure 4: Percentage of saturated and unsaturated methyl esters

The average chain length of methyl ester from the product also confirmed that the mixture was more of unsaturated C<sub>18</sub> esters. The catalytic activity of the catalyst sample was further demonstrated by comparing the chain composition of the feedstock with the methyl esters (see Figure 5). The feedstock was mainly comprised of oleic acid (64%) and 0% myristic acid.

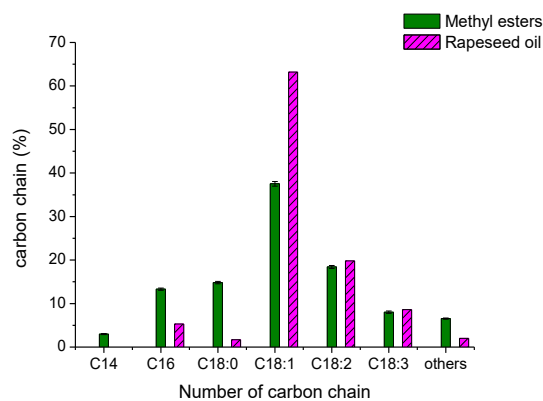


Figure 5: Distribution of methyl esters in product compared with the feed

In the product mixture the presence of myristate and particularly the substantial reduction in the percentage of oleic acid yielding methyl oleate is a clear evidence of cracking of the triglyceride molecules by the catalyst. The cracking of the triglycerides into methyl ester and other products in addition to carboxylic acids (FFAs) was enhanced by the catalyst. This is obvious in Figures 6 and 7 where thermal cracking of the same feedstock at the same temperature yielded only fatty acid without any methyl ester as revealed by and GC-MS chromatograms. In previous researches, the selectivity for saturated and

unsaturated methyl esters was not reported; that could be of industrial interest.

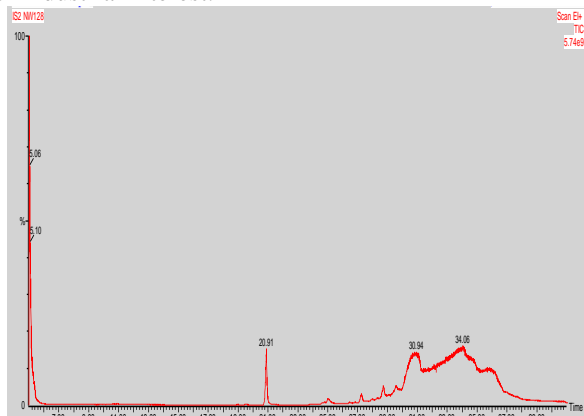


Figure 6: GC-MS chromatogram of thermally cracked feedstock

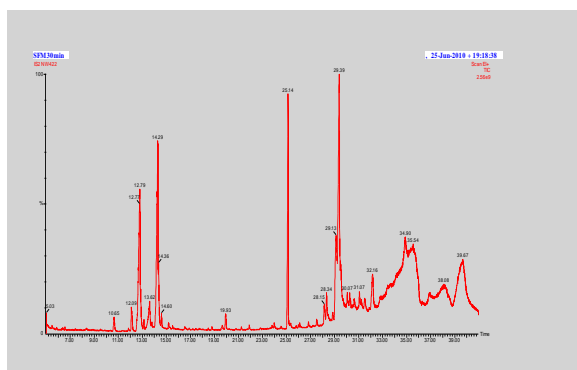


Figure 7: GC-MS chromatogram of thermocatalytic cracked feedstock

## CONCLUSION

Thermocatalytic cracking of triglycerides with a non-crystalline sulphated zirconia catalyst exhibited high activity for the production of biodiesel (methyl esters), methane, propane and hydrogen. This is in contrast to earlier reports that a crystalline phase is required for sulphated zirconia catalytic activity [14]. The maximum yield for methyl esters achieved here was 58%, which is higher than any selectivity for FAME from triglyceride by cracking as previously reported in the literature. An important secondary observation is that the selectivity for unsaturated methyl esters was mostly single double bond. Another important industrial chemical identified is a long chain unsaturated fatty acid alcohol, 1-Heptatriacotanol ( $C_{37}H_{76}O$ ). No previous study has reported the production of methyl heptadecanoate or the unsaturated fatty acid alcohol from the cracking of triglycerides. The

direct thermocatalytic cracking of triglycerides is thus a promising process for methyl ester (biodiesel) production, since the need for alcohol in the conventional transesterification process is entirely removed, and there are potential synergies with the cracking of oil. Using thermocatalytic cracking of triglycerides for biofuel production is feasible and can be sustainable and the degree of saturation of the methyl esters produced can be tuned.

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## Persian Abstract

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## چکیده

سوخت های بیولوژیکی منابع انرژی تجدیدپذیری هستند که اساسا با ترانس استریفیکاسیون اسیدهای چرب در حضور آنزیم و کاتالیست ها تولید می شوند. ترانس استریفیکاسیون بر استفاده از کاتالیست های هموزن باز قوی یا اسید قوی برای عملکرد بهتر استوار است، اما کاتالیست های هموزن با تنوعی از انواع فنی همراه است که استفاده ی آن ها را برای تولید بیودیزل محدود می کند. اگرچه اخیرا پیشرفت هایی در کاتالیست های هتروژن برای تولید بیودیزل از طریق ترانس استریفیکاسیون صورت گرفته است، جداسازی متیل استر از گلیسرول خام و بازیافت الکل هنوز موانع اصلی هستند. یک راه اصلاحی ممکن می تواند استفاده از thermocatalytic cracking تری گلیسریدها باشد. کاتالیست zirconia سولفات شده برای cracking کاتالیزوری دمایی تری گلیسریدها در دمای نسبتا پایین (270 °C) و فشار اتمسفریک ارزیابی شد. مشخص شد که کاتالیست نسبت به cracking روغن های گیاهی به متیل استرها فعال است. کاتالیست در این دما انتخاب پذیری متفاوتی را نسبت به تشکیل متیل استرهای اشباع شده و اشباع نشده نشان داد. بازده کاتالیزور متیل استر تحت این شرایط ۵۸٪ بود در حالی که ۸۰٪ محصول غیر اشباع بود. این امر امکان کنترل درجه اشباع محصول متیل استر را با انتخاب کاتالیست، برای تولید سوخت های با درجه ی اشباع بیشتر یا کمتر را برای بازارهای مختلف فراهم می کند. محدوده ی محصولات از گازها تا عصاره های میانی و گزینش پذیری بی همتا برای استرهای اشباع شده و اشباع نشده ممکن است یک مزیت مهم فرآیندی در این فرم از cracking کاتالیزوری باشد. همچنین یک الکل غیر اشباع زنجیره بلند مهم (۱-Heptatriacotanol) شناسایی شد. الکل غیر اشباع به عنوان یک ماده ی شیمیایی صنعتی شناخته شده است.