Catalytic Modification in Biofuel Transesterification to Control Reaction Yield and Metal Retention – A Study by Hyphenated Quadrupole Mass Spectrometry

N. Li, M. Elkadi, A.E. Pillay, S. Stephen

Abstract— **The object of this investigation was to examine the prospect of controlling reaction yield and metal retention *in vivo* by modification of the catalytic conditions of the transesterification process. Reforming catalytic treatment in this way could contribute to a deeper understanding of general biofuel production. The present study explored the addition of crown ethers to standard catalytic preparation of neem biodiesel (NaOH/KOH) and monitored the resultant impact of the revised treatment. Crown ether is depicted as a "cage-like" structure for entrapment of trace metals within the cage diameter. Crown ethers tend to bind metal ions if their ionic radii correspond to the cage size ranges of 260-320 pm for 18-crown-6 ether; and 170-220 pm for 15-crown-5 ether. The experimental results were compared with those derived from the unmodified treatment and from direct TBAH treatment. The accumulated data revealed that product yields and metal retention are strongly influenced by catalytic modification. Combined KOH/18-crown-6 treatment produced the best results. Metals were characterized by hyphenated mass spectrometry (ICP-MS), and a wide range of elements were detected in the μg/L range. Heavy metals and trace elements in biodiesel are undesirable because they can pollute the environment, clog fuel lines in vehicles, and damage hardware. Instrumental performance was validated by certified standards, and regular software was used to correct for background and matrix effects. Of considerable significance is the resultant diminished toxicity in the biofuel product following catalytic modification. Our work contributes to sustainable development, and provides useful information on advanced mechanistic theory associated with catalysed transesterification.**

Index Terms— **Crown ether, heavy metals, homogeneous catalysts, ICP-MS, neem biodiesel.**

I. INTRODUCTION

Reforming catalytic treatment of transesterification in biofuel production by addition of active chemical components to the reaction chamber is a relatively unexplored area in biofuels research. The present study examined the potential of enhancing biofuel production by combining standard catalysts NaOH/KOH with crown ethers. We found that revising the reaction conditions *in vivo* influenced yields and controlled metal retention in the biodiesel fraction.

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It is known that elevated levels of metals in biodiesel are undesirable and can damage machinery and pollute the environment [1]-[5]. There is, therefore, a growing need [6]-[8] to develop methods to produce high purity biodiesel with limited metal content.

Crown ethers play a role in activating the host catalyst, and are endowed with "cage-like" structures [9] to trap metal ions especially if their ionic radii correspond to the cage diameters [9]. In this way metal retention could be controlled. The basis of this investigation, therefore, involved development of novel *in vivo* methods of catalytic treatment [10] in neem biodiesel production to boost yields and limit metal retention. Routine production of neem biodiesel and the protocol affiliated with the process has been reported elsewhere by the authors [5] and will not be repeated here. Metals and trace elements were characterised using high performance ICP-MS (inductively coupled plasma mass spectrometry). ICP-MS is an instrumental technique renowned for its capacity to produce superior detection limits in trace elemental analysis [5], [11], [12]. Its highly sensitive capability ($<\mu g/L$) has been reported to exceed that of any other contemporary method of analysis [13]-[17]. To assess the extent of metal retention under modified catalytic treatment more than 25 metals/metalloids and toxic elements were determined. The outcome was compared with conventional NaOH/KOH treatment, and direct tetrabutylammomium (TBAH) treatment. The impact of our study and its potential benefit to sustainable development are discussed.

II. MATERIALS AND METHODS

A. Sample treatment / Catalysts

Neem oil purchased locally was used as feedstock for the biodiesel preparation. For purposes of comparison feedstock with elevated water content was also studied. A point to note is that water contamination of feedstock could lead to the production of by-products, e.g. soap, and subsequent failure to produce prolific yields. The production process itself essentially entailed acid-catalysed pre-treatment of the neem oil, followed by a base-catalysed transesterification step in the presence of methanol [5]. The catalysts employed were as follows: sodium hydroxide; potassium hydroxide; sodium hydroxide with 15-crown-5; potassium hydroxide with 18-crown-6 and TBAH. Certain parameters played a role in the choice of crown ethers. On account of the atomic size of Na^+ (190 pm), K^+ (266 pm) and cavity diameter of crown ethers [9], 15-crown-5 (170-220 pm) was introduced to the NaOH catalyst mixture; while 18-crown-6 (260-320 pm) was added to the KOH

solution. The isolated biodiesel fraction was washed several times in warm water to free it of impurities and finally dried in an oven at 100 °C for 2 hours to discard residual water. Treatment with TBAH was identical but excluded introduction of additives. The physical properties of the biodiesel fractions conformed to standard specifications [5].

B. Hyphenated mass spectrometry (ICP-MS)

Biodiesel samples were digested in mild acidic media using an industrial grade microwave oven and placed in an automated sampler for analysis by a Perkin Elmer SCIEX DRC-e ICP-MS. The solution containing the biofuel fraction was subjected to nebulisation and conveyed to a high-temperature core (~6000 K) where it was atomized and converted to ions corresponding to the elements of the sample. These ions were controlled by a quadrupole selection system and subsequently accelerated to a mass spectrometer for detection. For favourable performance the instrumental argon gas flow was 0.80 L/min. The technique is particularly sensitive for trace elemental determination [5], [12] and can achieve lower limits of detection in the ng/L range (sub-ppb) for most metals and metalloids. A distinct advantage was that small quantities of sample (200 μL) could be diluted for representative analysis. All samples underwent similar treatment and conditions of analysis were closely monitored. Standard procedures for background correction and elimination of interferences were followed. Suitable certified standards were used to calibrate the technique (Fluka 70007; 10.0 ppb per element). An internal standard was used to adjust for minor aberrations in instrumental measurements. The automated facility of the instrument permitted repeatable sample analysis and relative standard deviations for each measurement were automatically recorded by the instrument. Repeatability data produced relative standard deviations within 5% demonstrating that the performance of the system for aqueous samples was favourable.

III. RESULTS AND DISCUSSION

A. Reaction yield

The biodiesel yields from native feedstock (neem oil) containing diminished (0.066% H_2O) and elevated (0.97% H_2O) water content were examined. Water contamination clearly reduced the integrity of the "wet" samples and affected the corresponding results, producing lower yields in general. On the whole, treatment with KOH and 18-crown-6 produced the most favourable yields – 93.98% and 80.77% for both sample batches, respectively. Clearly, addition of crown ethers to the system plays a vital role and tends to increase the reaction yield. This could be attributed to the strong interplay of intermolecular forces between the cationic components of the host catalysts [18]. Unlike the way NaOH and KOH catalyze the transesterification reaction, crown ethers bind the host cations K^+, Na^+ by ion-dipole attraction prior to the reaction between KOH/NaOH with methanol as shown in Fig. 1. As a result of this, the hydroxide is more active to react with methanol to form the methoxide anion, CH_3O^-. In addition, the bulkiness of the crown ethers decreases the forces between CH_3O^- and crown ether-metal complex, which leads to increased

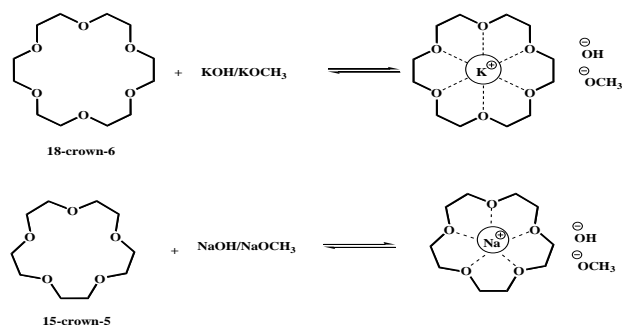nucleophilicity of CH_3O^-. The CH_3O^- anion is then more

Fig. 1: Hydroxides and methoxides solvated by crown ethers

freely available to react with the triglycerides.

B. Mechanism / Incomplete transesterification / Water contamination

During the production of biodiesel one of the main problems is the lack of completeness of the transesterification reaction [19]. Instead of complete conversion of triglyceride to glycerol and methyl esters (biodiesel), some of the triglyceride molecules undergo partial transformation and, as a result, are converted to diglycerides and monoglycerides. Under these conditions, a residual mixture of triglycerides, diglycerides, and monoglycerides, in various proportions, remains in the reaction chamber and the primary yield of the reaction is distinctly affected (Fig. 2).

Water contamination creates a setback. In the transesterification process, the methoxide (CH_3O^-) ions attack the carbonyl group of the reactant ester resulting in a more compact methyl ester (biodiesel) and an alcohol by-product. In the presence of water, saponification takes place, which leads to emulsification. The hydroxide ions produced under basic conditions can compete with the methoxide and attack the carbonyl group of the ester, resulting in the production of the metal salt or soap. If water could be eliminated, then there would be no soap formation. However, this is a practical impossibility. There is always some water present, and there will always be some soap formed when biodiesel is made (Fig. 3).
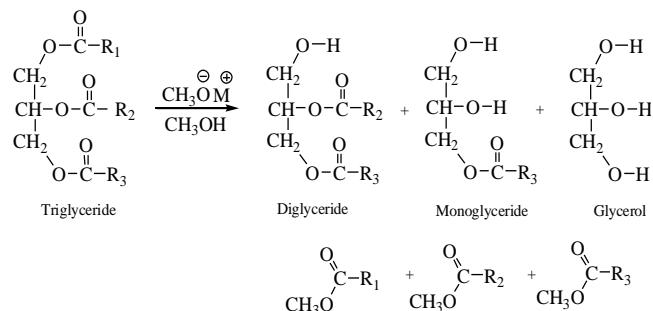

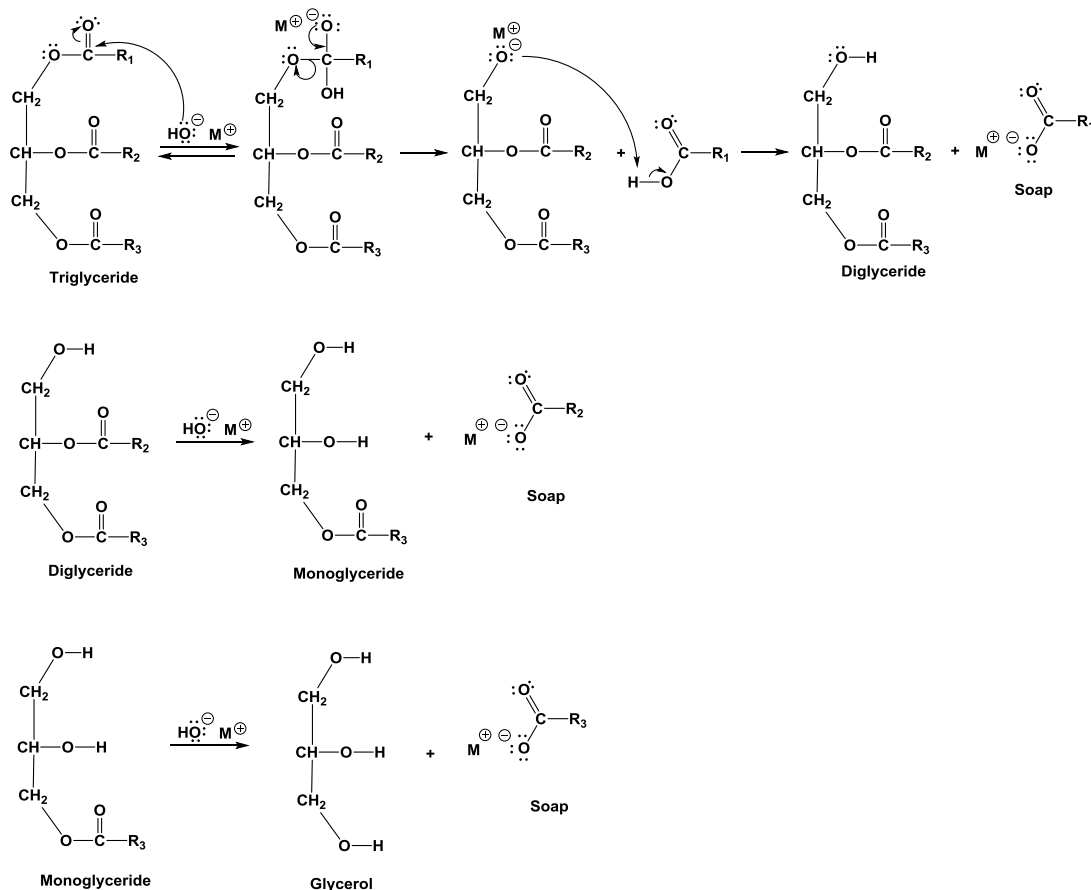Fig. 2: Reaction showing incomplete transesterification

Fig. 3: Mechanism of incomplete transesterification with soap formation due to water contamination

C. Metal retention

With regard to controlling metal retention the entire focus was on the behavior of the crown ethers and their reactive abilities. The crown ethers tend to trap metals with an ionic radius in their cage-size [9]. The crown ether-metal complex may subsequently reside in the biodiesel phase since they are soluble in biodiesel - and thus lead to a comparatively higher metal retention. However, if cage size ranges do not permit capture of metal ions, metals are transferred to the glycerol by-product, thus limiting metal retention in the isolated biodiesel fraction. Table 1 presents "cage" ranges and corresponding ionic radii of metals that fall within these ranges. It is clear from Table 1 that 15-crown-5 possesses the greatest potential to capture metals. This particular crown ether was combined with NaOH and as reflected in Fig. 4 treatment with this catalytic combination produced comparatively higher elemental levels, as expected. According to the data in Fig. 4 the concentrations of the majority of the elements were within 1000 μg/L. A few transition metals (Ti, Cr, Fe, Cu, Zn) and Pb occurred at higher levels, in the mg/L range.

It is evident from the data in Fig. 4 that the most promising results came from treatment with KOH/18-crown-6, which rivalled direct KOH treatment. Treatment with NaOH/15-crown-5 was not encouraging, simply because it led to greater metal entrapment according to the crown ether theory proposed above. Direct treatment with NaOH was also disappointing because it failed to minimise metal retention. The approach with TBAH produced elevated levels for undesirable elements: Bi, U, Cr, Ni, Se and Sb. Clearly, TBAH has not proved practical from the perspective of limiting metal retention and its use should be restricted.

D. Diminished toxicity - As, Cd, Pb and Hg

Environmental concerns play a vital role in biofuels development. Clean energy is the ultimate goal and the key motive is to promote sustainable living. There is, however, little point in using alternative fuel to mitigate climate change when toxic pollutants such as As, Cd, Pb and Hg are present at appreciable levels in the biodiesel product. It is, therefore, crucial to limit toxic metal concentrations in the biodiesel fraction. Our results in Fig. 4 clearly show that catalytic modification with KOH/18-crown-6 played a strong role in minimising toxic metal/metalloid levels and produced the most favourable results. Restriction of the metal content of the biodiesel fraction implies that these toxic elements would have transferred to the glycerol waste product. Prudent waste disposal, therefore, becomes an important consideration. Arsenic at abnormal levels is a known danger to our natural environment. Arsenic was present at ultra-trace levels (< 0.1 μg/L) in the biodiesel fraction linked to KOH/18-crown-6 treatment. The highest level of As emerged from NaOH treatment, which was more than a factor of 40 above the combined KOH/18-crown-6 result.

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Table 1: "Cage" range of crown ethers and ionic radii of elements [20]

18-crown-6 (CE/6)			260-320 pm	
15-crown-5 (CE/5)			170-220 pm	
Elements	Oxidation state	Ionic radius /pm	Diameter /pm	
Na	1+	95	190	CE/5
K	1+	133	266	CE/6
Ti	2+	90	180	CE5
V	2+	88	176	CE/5
Cr	2+	84	168	CE/5
Cu	1+	96	192	CE/5
Rb	1+	148	296	CE/6
Sr	2+	113	226	CE/5
Pd	2+	85	170	CE/5
Ag	2+	89	178	CE/5
	1+	126	252	CE/6
Cd	2+	97	194	CE/5
	2+	93	186	CE/5
Sb	3+	92	184	CE/5
Ba	2+	135	270	CE/6
Hg	2+	110	220	CE/5
Pb	4+	84	168	CE/5
Bi	3+	108	216	CE/5
Th	4+	94	188	CE/5
U	4+	89	178	CE/5
	3+	102.5	205	CE/5

Cadmium is another notorious toxic element that has been at the forefront of environmental issues and tends to function as hazardous pollutant when emitted to the atmosphere. Here again, treatment with KOH/18-crown-6 gave the best results, and the Cd concentration from this approach compared to the highest detected level (NaOH/15-crown-5) in Fig. 4 was significantly lower, and differed by a factor of ~ 3. Mercury in the form of methyl mercury could be deleterious to the environment especially if biodiesel waste products are dumped into landfills and earth-pits. Acquisition of diminished levels of Hg under these novel experimental conditions represents a highly useful contribution to research of this nature. The mercury level with KOH/18-crown-6 treatment was promising and lower by a factor of ~ 2 compared to the TBAH study, which produced the highest mercury levels. It is well known that Pb in exhaust fumes could pose a definite threat to the environment. Lead is noted to cause neuro-disorders so minimising its levels in biofuels by any means is beneficial. The lead levels in our study with KOH/18-
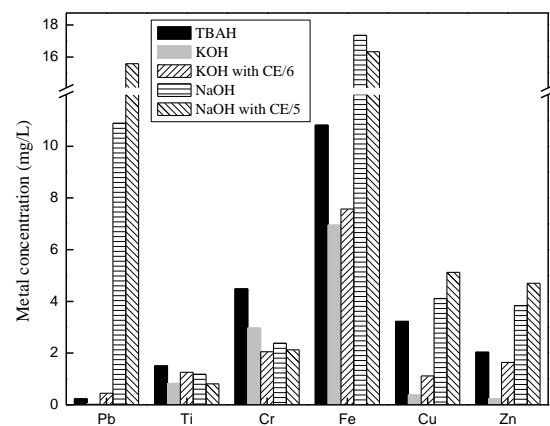
crown-6 compared with other treatments in Fig. 4 diminished appreciably up to a factor of ~ 18. Achievement
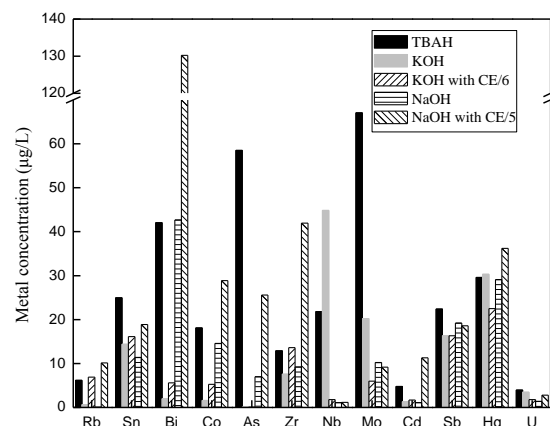
(a)
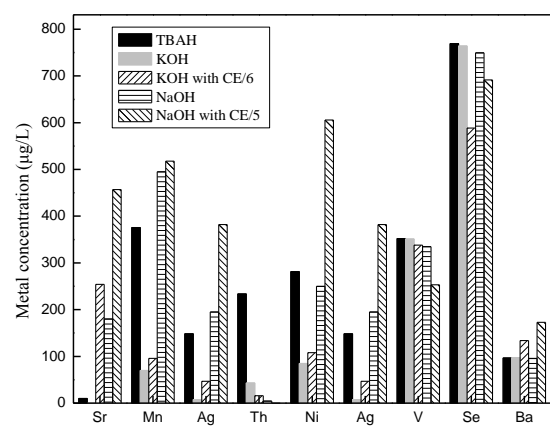
(b)

(c)

Fig. 4: Metal concentrations in the biodiesel fraction corresponding to various catalytic treatments. NaOH/15-crown-5 results are derived from the water contaminated sample.

of overall diminished toxicity by reforming the catalytic conditions of transesterification represents a distinct improvement to the quality of the biodiesel product.

E. Impact of the study

The significance of this study is twofold. Firstly, our work has made a practical contribution to mechanistic theory relating to the behaviour of crown ethers and metal capture (*in vivo*) with standard catalysts NaOH/KOH. Secondly, our research covers a novel area associated with manipulation of the conditions of transesterification to concurrently restrict metal retention and improve yields in neem biodiesel. Crown ethers tend to activate the host catalysts and capture metals in their "cage-like" structures and this combined feature represents the novelty of our study. The present investigation could be extended to biofuel production in general and could reduce the need for de-metallisation procedures. The impact to sustainable development is equally important. The use of crown ethers to improve the product yield (and quality) by activating standard NaOH/KOH is relatively cost-effective and can easily be developed on a wider scale. In terms of sustainable living, reducing metal content in the biofuel product by appreciable factors is a key fulfilment. In particular, diminished toxicity by the aforementioned catalytic modification affects environmental issues and is of benefit to society in general. Interestingly, improved viscosity was also attained with treatment with KOH/18-crown-6, which could be due to a higher purity product.

IV.   CONCLUSION

Our study was successful in developing an alternative fuel with improved characteristics. The most notable feature of our research is that it can be extended to general biodiesel production with a variety of feedstock ingredients. Another promising aspect is that the product derived from treatment with KOH/18-crown-6 was higher in purity and possessed superior physical properties, including viscosity. An interesting aspect is that the mechanism governing metal capture in crown ether could be extended to other crown ethers and similar chemical species. This area could be a subject for future study. Attaining minimal elemental toxicity is an attractive feature in biofuel development. Clearly, reduced metal retention in the isolated fuel fraction is the key attraction and novelty. Our work promotes sustainable development and environmental well-being by generating an alternative fuel with diminished toxicity.

ACKNOWLEDGEMENTS

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