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Comparative Study of Heterogeneous Transesterification of Crude and Degummed Kapok Oil

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Authors' contributions

This work was carried out in collaboration between all authors. Author HI designed the study. Author DCN carried out the experiments supervised by author IAMD. Author DCN wrote the manuscript edited by authors HI and IAMD. All authors read and approved the final manuscript.

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ABSTRACT

Crude and degummed kapok oils were transesterified with heterogeneous catalyst (calcium oxide) to determine its potency for biodiesel production in Nigeria. Calcium oxide catalyst was synthesized by supporting 15% hydrated lime on 85% by weight of alumina. The crude oil was degummed by heating it to 80°C with auto phosphoric acid for 30 minutes. It was then esterified to reduce free fatty acid content to 0.5 mgKOH/g. Some quantity of crude oil was also esterified as in degummed oil. The two oil samples were transesterified with 25% methanol (weight % of oil) with catalyst loading of 0.4%, 0.6%, 0.8%, 1.0% and 1.2% (weight of oil). The methyl esters yield of crude oil were; 5.0%, 32.92%, 58.97%, 48.39% and 53.79% and that of degummed were; 58.97%, 72.48%, 85.25%, 88.9% and 86.78%. The degummed oil had higher methyl esters content yet not up to minimum European Union Standard of 96.5%. It is therefore recommended to degum crude kapok oil before transesterification.

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1. INTRODUCTION

Biodiesel is an alternative diesel fuel consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Biodiesel is a promising alternative fuel that can be derived from waste oil, animal fats or vegetable oil that has been converted into methyl esters through transesterification with methanol [1]. Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety [2]. Base catalyzed transesterification is the most commonly used technique as it is the most economical process [3]. According Ibrahim [4], the reaction is catalyzed mostly by base (such as sodium hydroxide, potassium hydroxide or sodium methoxide) and in some cases strong acid such as sulphuric acid but the reaction rate is as low as 4000 times as base reaction. Presently, a lot of heterogeneous catalysts have been formulated that are more effective than the homogeneous catalysts [4].

Most biodiesel is made from edible sources like soybean oil, rapeseed oil, palm oil, etc. However, there are large amounts of fats and oils that are not edible that could be converted to biodiesel at lower cost. The problem with processing these waste oils is that they contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst without refining. Methanol and an alkaline catalyst are also used in the production of biodiesel. However, production costs are still rather high, compared to petroleum-based diesel fuel due to processes involved. The use of solid heterogeneous catalyst in biodiesel production could reduce its price, becoming competitive with diesel also from a financial point of view. Ecological, political and economic concerns over petro diesel are the drivers behind biodiesel production from edible, non-edible oils and fats [5]. Simple straight chained mono-alcohol such as methanol, ethanol and propanol are used in producing biodiesel. Methanol is most commonly used in the commercial production, since it is generally less expensive than other alcohols, but ethanol prevails in regions such as Brazil where it is less expensive than methanol [6]. Methanol is more reactive and the fatty-acid methyl esters (FAME) produced are more volatile than fatty-acid ethyl esters (FAEE) [7].

In the course of this investigation, calcium oxide (CaO) catalyst was prepared by mixing hydrated lime with aluminum oxide in the ratio of 15:85 (15% active ingredient) in distilled water. The mixture was heated to dryness on a magnetic stirrer. The dried mixture was calcined at a temperature of 700°C for 1 hour 30 minutes. The following analyses were carried out on it: SEM and FTIR. The calcium oxide catalyst was used to catalyze the transesterification of crude and degummed kapok oils to biodiesel. The biodiesel products were characterized using GC-MS machine.

2. MATERIALS AND METHODS

The materials require for this study include; 500 mL beaker, 250 mL conical flasks, stirring rod, magnetic stirrer and follower, crucibles, aluminum oxide, hydrated lime obtained from pilot plant of National Research Institute for Chemical Technology, Zaria and Gallenkamp muffle furnace, scanning electron microscope, SEM, Fourier transform infra-red, FTIR, *Ceiba pentandra* seed (kapok) oil, methanol, isopropyl alcohol and potassium hydroxide.

2.1 Preparation of Catalyst

15 g of hydrated lime was dissolved in 500 mL beaker containing about 300 mL distilled water. After thorough mixing 85 g of alumina was added and stirred [7]. The mixture was evaporated over a hot plate magnetic stirrer. The dried mixture was loaded into crucibles and was calcined in a Gallenkamp muffle furnace at 700^{o}C for 90 minutes. The calcined catalyst was grounded into powder and subjected to different characterization methods.

2.2 Characterization of the Catalyst

Samples of the catalyst was taken to SEM and FTIR machines for particle size, pore area, chemical components present and pore volumes.

2.3 Degumming of Kapok Oil

Crude kapok oil was degummed by heating the oil to 80°C, mixed with water and autophosphoric acid (5% vol.) and stirred for 15 minutes on Gallenkamp hot plate magnetic stirrer [8]. Then, the mixture was poured into the separating funnel and allowed to stand for 30minutes before it was separated and esterified.

2.4 Transesterification

0.2 g of the catalyst (which was 0.4% mass of oil) was mixed with 25 g of methanol. This mixture was poured into 50 g of crude kapok oil heated at 60°C for 60 minutes. At the end of the 60 minutes the product was filtered using sintered funnel. Using the same method, other transesterifications were carried out with 0.6, 0.8, 1.0 and 1.2% catalyst loading, keeping the mass of oil and methanol constant at 50 g and 25 g respectively.

2.5 GC-MS Analysis

The methyl esters, free fatty acids, carbonyl compounds, alcohols, hydrocarbons and other impurities content of each sample was determined by dissolving 2 mL of biodiesel sample in n -hexane in a sample bottle. This sample bottle was inserted and run in the GC-MS machine, GCMS-QP@)!) PLUS SHIMADZU/JAPAN in the Quality Control Unit of NARICT, Zaria. The machine vaporized the sample and separated it into different compounds found in the solution and also quantifies of each component.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

A characteristic vibrational mode was observed in the range 3500 and 3000 cm^{-1} as shown in Fig. 1 of broad spectra band. The spectrum was a weak absorption band due to O-H stretching vibration of water molecules [9]. Prabhavathi et al. [9] recorded 3423 cm^{-1} for CaO due to its bonding with hydroxyl groups from moisture. It can be seen that the stretching vibration of OH group was shifted from 3393 cm^{-1} to 3421.03 cm^{-1} which could be due to chemical interaction between OH and CaO. This is supported by Cooke, [10] 3600-3200 cm^{-1} for O-H for strong and broad spectra. This confirmed the presence of calcium oxide, CaO. According to Simonescu [11] carboxyl peak for unloaded biomass is at 1638 cm^{-1}but shifted to 1640.9 cm^{-1}.This increase in the wave number of the peak could be the characteristic for interaction of C=O group from carboxylic acid functional group with Ca ions of CaO. According to Djebaili et al. [12] the IR spectroscopy in the range 400–1000 cm^{-1} can be used as stand easy tool to distinguish the presence of transition Al_2O_3 phases on oxidized high temperature materials and to determine whether γ, δ or α-Al_2O_3 are present. The spectra with wavelength of 640.84 cm^{-1} falls in the range of α-Al_2O_3 in the range 656.24-459 cm^-1 [9] indicated the presence of α-Al_2O_3as shown in Fig. 1.

3.2 Scanning Electron Microscope (SEM) Results

The average grain size of the catalyst sample was 2501.64 nm (2.5 µm) which was smaller in size compared to that synthesized on ratio 1:4 by Ibrahim [6] with particle size of 62.25 um. This indicates that the less the quantity of active component the less the particle size one would get. The pore surface area of the catalyst was 0.1 $µm^2$ which is also higher than 0.0100 $µm^2$ synthesized from ratio 1:4 by Ibrahim [6]. Fig. 2 shows the SEM image and pore size distribution of the synthesized calcium oxide catalyst. Gummalla et al. [13] claimed that the catalytic activity of a catalyst depends on the shape and size of the nanoparticles. The particle size of this catalyst is in nanometer range mostly between 407.58 and 3470 nm as shown in Fig. 2b. It has pore surface area of 0.1 $µm^2$ as shown in Fig. 2c.

3.3 Methyl Esters Yield and Impurities

In both crude and degummed, the methyl esters yield increased as the catalyst loading increased with degummed oil having upper hand as shown in Fig. 3. The methyl esters yields from the degummed oil were higher for all the five productions. The degummed oil had the highest yield of 88.9% in 1.0% catalyst loading which could be the optimum catalyst loading. The crude oil had the highest methyl esters yield of 59% in 0.8% catalyst loading. Tukur and Ibrahim [14] obtained 78.2% methyl esters yield from crude kapok oil with 1:4 CaO/Al_2O_3.This indicates that the higher the quantity of active component; CaO the higher the strength of catalyst. The claim of higher performance by smaller particle size by Gummalla et al. [13] does not applied here. The curves of these productions may indicate the maximum catalyst loading for the processes. The highest yield of methyl esters content obtained from the processes could not meet the minimum standard of European Union of 96.5% [15]. There are some components of kapok oil that could not be converted to methyl esters such as hydrocarbons.

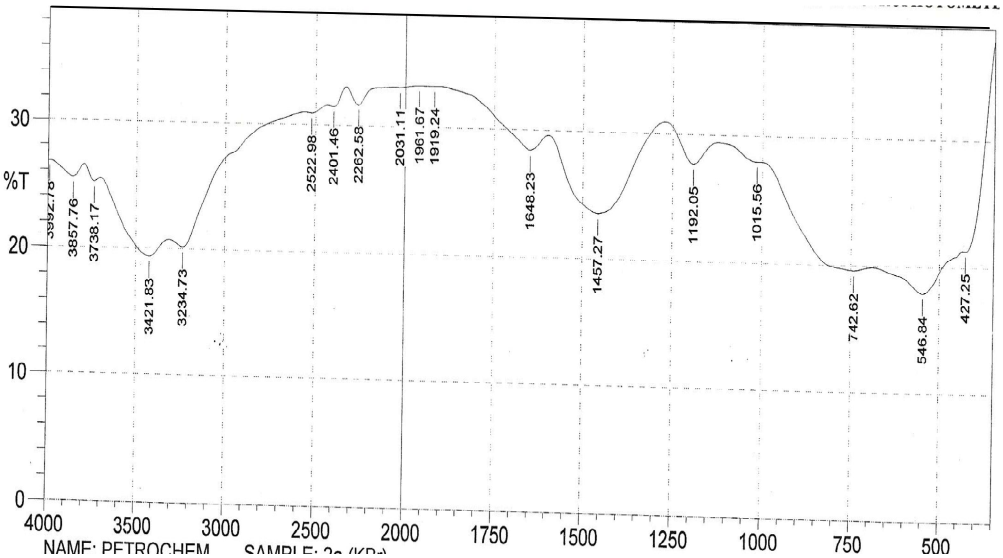
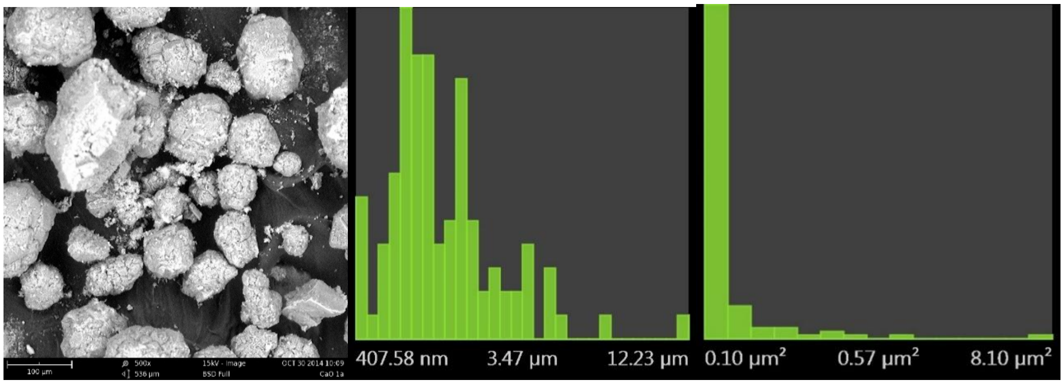


Fig. 1. Fourier Transform Infra-Red (FTIR) spectra of CaO/Al_2O_3 catalyst



(a) Particle image **(b) Particle size** **(c) Pore areas**

Fig. 2. SEM images of synthesized calcium oxide catalyst

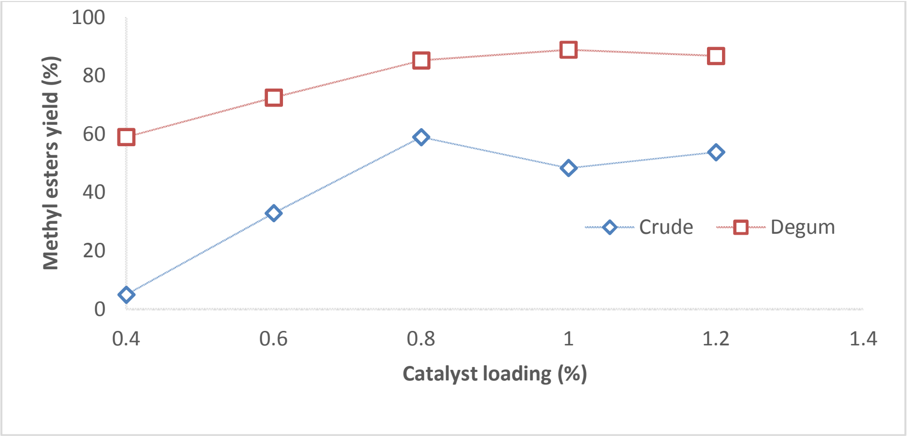


Fig. 3. Comparison of methyl ester yield from crude and degummed kapok oil

The acid content of the crude was higher than that of the degummed oil in the 0.4% catalyst loading but the subsequent productions showed alternating rise and fall of acid content as shown in Fig. 4. Overall, the acid content of crude oil biodiesel samples was higher than that of the degummed samples. Probably, some of the fatty acids were removed by degumming process.

The carbonyl compounds content of the degummed generally decreased progressively from 11.12% in 0.4% to 0.46% in 1.2% catalyst loading. However, there was a rise in carbonyl compound content after reaching the minimum in 1.0% to 1.2% catalyst loading as shown in Fig. 5. The crude oil biodiesel had zigzag carbonyl compounds content with higher value in the overall. The carbonyl compounds in the two routes were chiefly alkanals and alkanones. The tendency of polymerization is higher with the crude products than degummed products.

Hydrocarbons content of degummed oil biodiesel decreased progressively with increase in catalyst loading as depicted in Fig. 6 from 16.74% in 0.4% catalyst loading to 0% in 1.2% catalyst loading. But on the other hand, the hydrocarbon content in the crude oil biodiesel increased from 0.47% in 0.4% catalyst loading to a maximum of 29.44% in 1.0% catalyst loading and fell to 27.8% in 1.2% catalyst loading. Therefore, to reduce the hydrocarbon content in the kapok oil biodiesel it is better transesterified from its degummed oil.

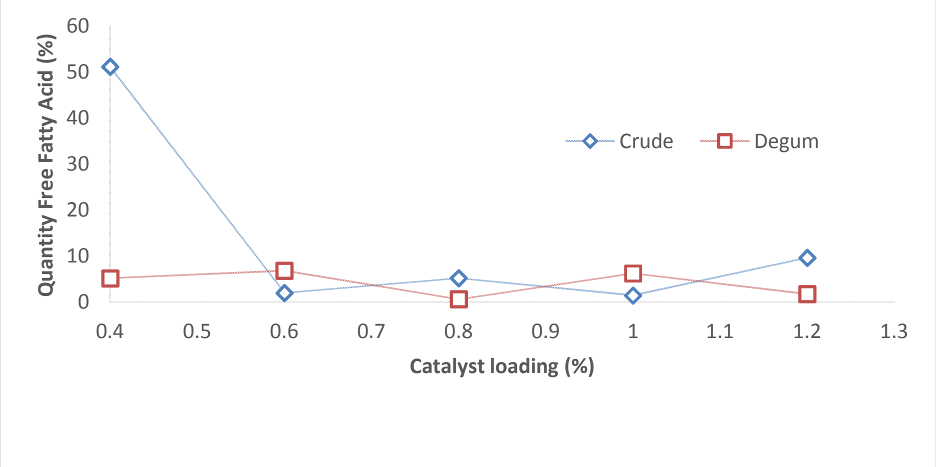


Fig. 4. Comparison of acid content in the crude and degummed oil biodiesel

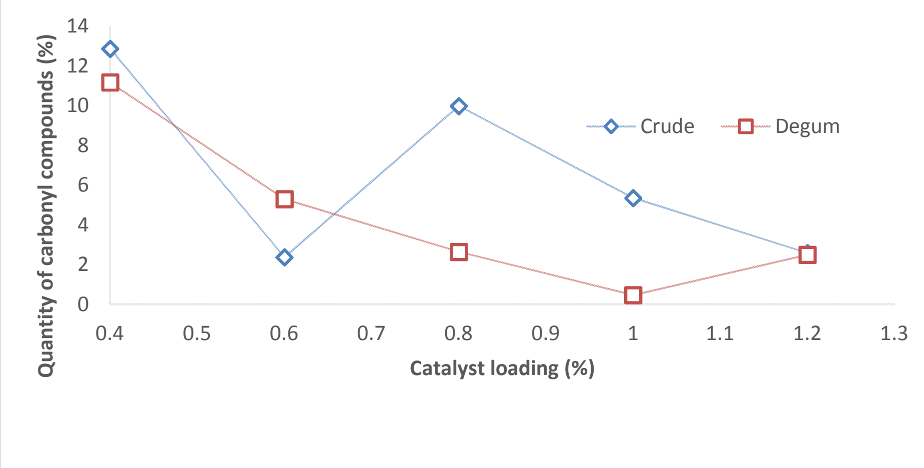


Fig. 5. Carbonyl compounds in the crude and degummed biodiesel samples

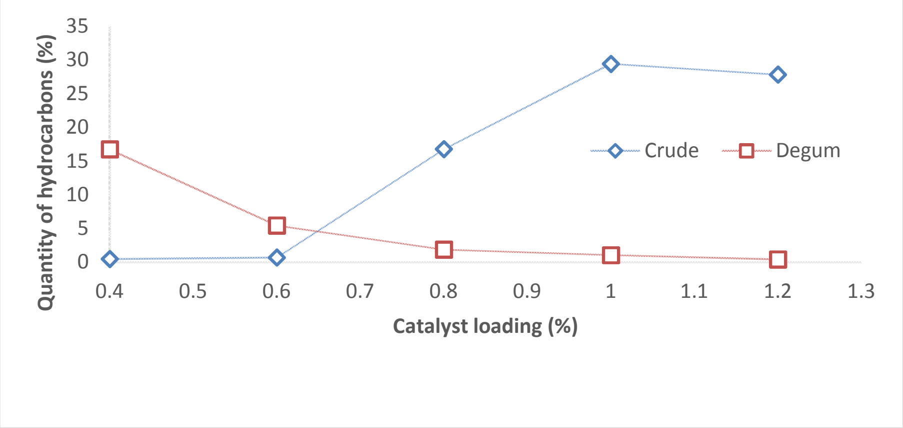


Fig. 6. Hydrocarbons content in crude and degummed oil biodiesel samples

Generally, the alcohols content of crude oil biodiesel was higher than that of degummed as shown in Fig. 7. The product of 0.8% and 0.4% catalyst loading of crude and degum respectively had zero alcohols. The highest alcohol content of crude oil was 15.79% in 0.6% catalyst loading and that of the degummed was 9.9% in 0.8% catalyst loading. The effect of catalyst loading and refining of the kapok oil on the alcohol content on its biodiesel is difficult to delineate as observed in this study. Hence, alcohols content does not really depend on either the refining of the oil or the catalyst loading. This result is similar to that of crude kapok oil biodiesel produced by Tukur and Ibrahim [14].

Some impurities like compounds containing sulphur, nitrogen, phosphorous, halogens and metals such as boron are classified as other impurities. Their quantity was small even negligible in the 0.8% to 1.2% catalyst loading in degummed oil biodiesel samples. The highest quantity of other impurities in the degummed kapok oil biodiesel was 7.5%. Generally, their quantity decreased as the catalyst loading increased, but crude oil biodiesel samples had higher content with 45% in 0.6% catalyst loading as shown in Fig. 8.

By degumming the oil and using higher catalyst loading, lowers (if not eliminate) the quantity of impurities in the product. In all degummed kapok oil had better biodiesel products and also the catalyst loading of 1.0% appeared to be optimum value for used in biodiesel production from this vegetable oil.

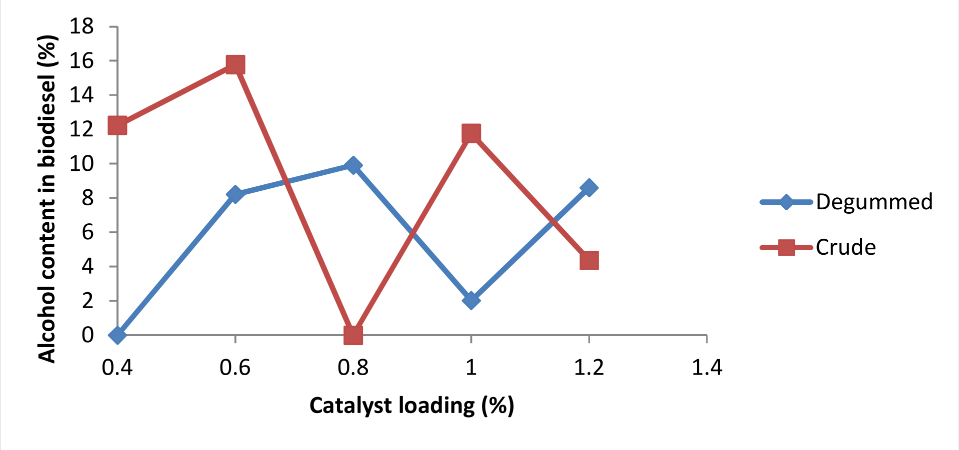


Fig. 7. Alcohols content in crude and degummed oil biodiesel samples

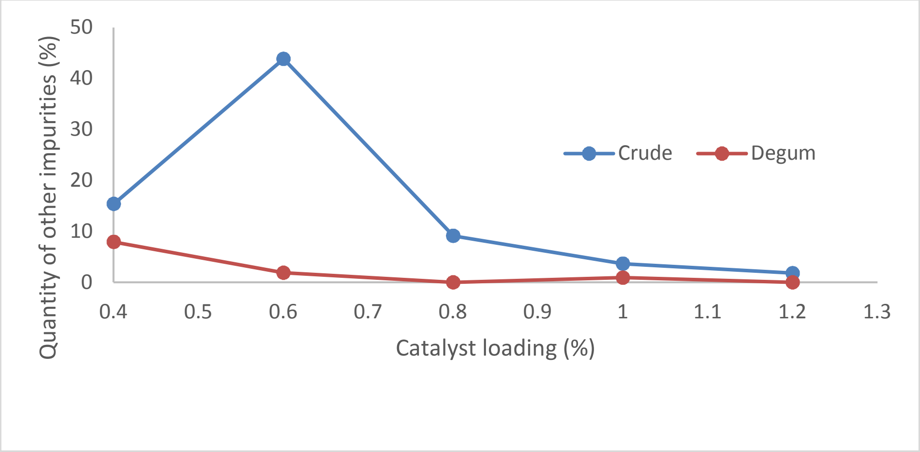


Fig. 8. Other impurities in crude and degummed oil biodiesel samples

4. CONCLUSION

Calcium oxide catalyst was successfully synthesized from the hydrated lime and alumina in the ratio of 3:17 (making 15% active ingredient). The particle size of this catalyst was smaller than that synthesized with 20% active ingredient by Tukur and Ibrahim [14]. The synthesized catalyst was found to be effective in biodiesel production with kapok oil (though less than 20% active ingredient) especially with degummed oil. The degummed kapok oil methyl esters yields were higher than the corresponding crude oil. The quantity of side products such as carbonyl compounds, alcohols and compounds of alkyl halides, alkyl metals, sulphur, nitrogen and phosphorous in the products fall with increased in catalyst loading.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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