Tuning Reaction Conditions to Enhance Catalytic Performance of Solid Ion-Exchange Resins Catalysts

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Abstract:- Recently, environmental, social and sustainability issues associated with use of fossil-based fuels are generating much concern and interest for the development of renewable energy. Catalyst design and development is critical and occupying central position for successful conversion of renewable feedstock to renewable fuels. In this work, optimization of reaction parameters that influences catalytic performance particularly biodiesel yield and catalyst reusability were tailored to enhance catalytic activities of basic anionic (Amerlyst-A26) and acidic cationic (Amberlyst-36) ion-exchange resins in transesterification of vegetable oil with methanol to biodiesel using both conventional and autoclave biodiesel synthesis. Basic anionic Amberlyst-A26 catalyst has demonstrated great potential for biodiesel synthesis with Sunflower oil than the acidic cationic Amberlsyt-36 resin using the conventional-round bottom flask method. Biodiesel yield >90% was obtained at temperature as low as 40 ^{o}C and a yield >75% within 1 hour at 50 ^{o}C. The catalyst showed higher degree of reusability by losing only 19% of its original activity after thirteen cycles. Conversely, autoclave biodiesel synthesis carried out using both catalysts revealed that the acidic Amberlyst-36 is more active under severe reaction conditions of autoclave. Hence, polymeric resins are viable active solid catalyst for biodiesel synthesis capable resisting leaching of active sites and loss of activity during biodiesel synthesis provided the right reaction conditions are explored.

Keywords:- *Heterogeneous Catalyst; Leaching; Biofuels; Biomass valorization; Reaction condition; Environment*

I. INTRODUCTION

Biodiesel is at the moment seen as alternative to petroleum diesel due to its inherent potentials such as renewability, sustainability, biodegradable nature and environmentally benign [1]. Characteristics of biodiesel closely resembles that petroleum diesel hence could be used on diesel engine without much modification. Despite the significant development of biodiesel industry witnessed over the years, catalyst design and development is still a pressing issue. There has been effort to replace the catalytically active but corrosive basic and acidic homogeneous catalysts with a more robust heterogeneous solid [2-4]. Consequently, solid catalysts (Heterogeneous catalyst) are now seen as possible replacement to homogeneous liquid catalyst as results of their less or zero corrosive properties, reusability and very high economic value and environmentally benign. Metal oxides of group two such as CaO, MgO and SrO have shown interesting results [5,6] and some transition and rare earth metals [7,8]. The metal oxides provides adsorptive site due their Lewis acid-Bronsted base nature hence activity depends on the strength of those sites [9]. Other heterogeneous catalysts that were found active are Zeolites and hydtrothalcites [10,11]. Despite the remarkable performance recorded in the use of these materials, leaching of the catalyst and consequent loss of activity remains a fundamental challenge [12,13].

The microporous polymeric structure of ion exchange resins, commonly derived from polyvinyl and styrene possesses a suitable surface area and active sites that are acidic sulphonic group or basics hydroxyl group. These groups function like the Bronsted acid or Lewis base surfaces providing active surfaces that catalyses transesterification of biomass vegetable oil to biodiesel with a minimal leaching of active phases. Investigation and studies have revealed that the property of ion exchange resins is attributed to their ability to swells in liquid medium and hence exposing their active sites to reactants for easy and rapid reaction [14]. The level or density of cross linking, particle size as well as size and diameter of the pore are also important factors that shape and determine the catalytic behaviour of resins [15,16]. Acidic cationic exchange resins have demonstrated great potentials in decreasing free fatty acid level of some oil such as waste cooking oil by catalysing esterification reaction which would have been done using homogeneous catalysts that are not environmentally benign and reusable [17,18]. This has improved the economic viability and commercialization of biodiesel synthesis. The catalytic properties and behavior of the acidic resin was connected to their properties which includes size and diameter of the resins pore and large surface area. Basic anionic resins have shown some promising results in the use of alternative renewable feedstock such as microalgae to boost biodiesel industry [19] and also in the conversion of the normal vegetable oil to biofuels [20,21]. Homogeneous catalyst CH_3ONa mixed with little quantity of anionic resin has shown synergic effects leading to promising results in the synthesis of biodiesel from vegetable oil. The results obtained were as a result of the regeneration of active catalytic site in the basic environment [22].

In the conventional biodiesel synthesis in the laboratory using heterogeneous catalyst, the process is carried out largely using the round bottom three-necked flask method with a stirrer. The miscibility of the oil-methanol phases was improved in many instances using vibration emanating from sound wave as against the known practice of using stirrer in the conventional method of transesterification reaction process to biodiesel. The process tends to shorten the conversion period or reaction time, methanol and energy consumption as well as catalyst loading and enhance conversion as well as biodiesel yield [23]. More so, autoclave biodiesel synthesis is also another approach that causes rapid conversion of the reactants (oil and methanol) under the influence high pressure with a consequent reduction of oil-methanol ratio and enhanced biodiesel yield. The autoclave stringent condition of high pressure and temperature causes rapid breakage of triglyceride bond and significantly increase reaction rate and reduce reaction time and the use of much catalyst amount to enhance biodiesel yield [24,25]. In this method, methanol and the autoclave system remains the only source of the vapour pressure. The autoclave system being a closed system has advantage of minimising the rate of alcohol loss even at high temperatures compared to the conventional method [26]. The method has proved useful and suitable for biodiesel synthesis. Thusahari et al., 2019 [27] demonstrated the use of autoclave reactor synthesis to generate biodiesel and has recorded maximum yield of 89.8% after 3 hours. The performance partly was attributed to high acid density from hydrophilic groups bonded to hydrophobic carbon network of the catalyst system.

In this work, Sunflower oil was trans esterified to biodiesel using some basic anionic and acidic cationic resins as heterogeneous solid catalysts. Conventional and autoclave methods of synthesis are explored and compared. Influence of reaction conditions, catalyst stability and reuse are also investigated to fully reveal their catalytic potential. The biodiesel yield progress was monitored using quantitative 1H NMR.

II. MATERIALS AND METHODS

A. Reagents Used

Sodium hydroxide (97%) and methanol (99.7%) were obtained from Fisher Scientific and Sigma-Aldrich respectively, edible soybean oil commercial grade was obtained from TESCO groceries shop in Dundee, Scotland United Kingdom. Basic anionic resin Amberlyst-A26 in hydroxide (OH^-) form and Acidic cationic resin Amberlyst-36 in acidic form (H^+) form were purchased from Sigma-Aldrich. Table 1 below shows some of the physical properties of the resins.

B. Catalyst Activation

Both Amberlyst-A26 and Amberlyst-36 were activated prior to their usage for transesterification reaction by ion exchange process using 1M NaOH and 1M H_2SO_4 respectively overnight. The activated catalysts were washed off using methanol to remove physically adsorbed NaOH and H_2SO_4 respectively then filtered and dried.

C. Conventional Synthesis of Biodiesel

A three-necked round bottom flask (250 ml) reactor with a reflux condenser attached and caped with glass stoppers and stirring system containing 10g of soybean oil was used. The reaction mixture was kept agitated by stirring with a magnetic stirrer kept at the desired rate on hot plate. Required catalyst loading and methanol ratio was measured and added to the flask while stirring as soon as desired temperature was attained. As soon as the temperature was set timing started and at specific intervals samples were collected into small vials using pastures pipette and dissolved methanol was removed by drying in the hood and triglyceride conversion measured using quantitative ^{1}H NMR on 400MHz using a formula thus [28]:

$$C = [2A_{CO2CH3}/3A_{\alpha\text{-}CH2}] \text{ X } 100.$$

Where C = vegetable oil to biodiesel Conversion
$A_{\text{-}CO2CH3}$ = proton due to biodiesel methoxy group integration value.
$A_{\alpha\text{-}CH2}$ = proton of the methylene structure from vegetable oil integration value.

D. Autoclave Synthesis

Required amount of the catalysts and methanol were measured and added to the autoclave reactor containing 10g of oil. The autoclave rector was kept in the oven at the appropriate reaction temperature and 3-10 bars methanol vapour pressure for 24hrs.

III. RESULTS AND DISCUSSION

A. Assessing Behavor of the Catalyst Systems in the Biodiesel Synthesis

The catalyst systems were subjected to transesterification reaction for screening using different vegetable oil-to-methanol ratio and percentage (%) yield was monitored as indicator for evaluation of catalytic behavior. The test was done at constant temperature of 60 °C in sunflower oil and 1g catalyst amount for 5 hours throughout the test. Figure 1a and Figure 1b respectively shows the trend and pattern of the results obtained and could be used to compare the catalytic activity of the anionic and cationic relatively.

The Amberlyst-A26 catalyst system gave a maximum conversion >90% at oil methanol ratio of 1:60 at 60 °C in 5 hours. Conversely, Amberlyst-36 yielded 12% biodiesel using 1:18 oil-methanol ratio at same temperature and duration of the test. Despite the fact that less sunflower oil was required for Amberlyst-36 when compared to Amberlyst-A26 catalyst, the results revealed that Amberlyst-A26 anion-exchange resin is more active relatively. Interestingly, although the result shows that the highest and maximum conversion was obtained with Amberlyst A-26 using 1:60 vegetable oil-methanol ratios, good triglyceride conversion of 69% was recorded with 1:20, 53% with 1:12 and 27% with 1:6 vegetable oil-to-methanol ratios respectively. The results revealed some improvement when compared to what was observed in a related work [16,17,20]. It is also important to further observe that the results suggest the catalyst system Amberlyst-A26 is very catalytically active at low vegetable to methanol ratio indicating uncommon behaviour of basic heterogeneous catalysts. More so, the dramatic change observed when vegetable oil to methanol ratio is varied corroborates the importance of this factor to synthesis of biodiesel via transesterification reaction.

Hence, the results suggest that performance of heterogamous catalyst systems in biodiesel synthesis could be enhanced through tailoring and careful choice of oil-to-methanol ratio. In practice, oil-methanol ratio in excess of the stoichiometric 1:3 ratio is used to enhance the rate of triglyceride conversion to biodiesel. The Amberlst-A26 catalyst sustained a steady increase in triglyceride conversion with increase in vegetable oil to methanol ratio up to ratio of 1:60, conversely, Amberlyst-36 performance in the conversion of triglyceride to biodiesel dropped after 1:20 and a slightly increased at 1:40.

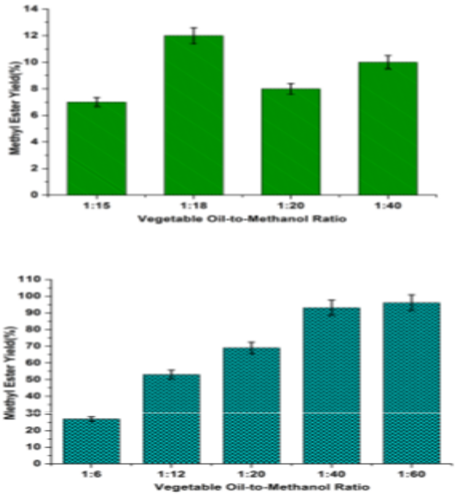

Fig. 1 showing influence of methanol consumption on the methyl ester synthesis as index for catalytic activity **(a)** using Amberlyst-A26 and **(b)** using Amberlyst-36

Consequently, the robust catalytic activity of the Amberlyst-A26 as results of its active site that are strongly basic and easy accessible during reaction process and couple with its suitable particle size, large surface area and pores as shown by the physicochemical properties of Table 1. The findings in this study compares favourably with what Feng, et al. (2010) [14] reported. More so, the superiority of activity shown by the Amberlyst-A26 is as a result of the high affinity of the anion resin basic site surface for the methanol during transesterification reaction when compared to that shown by the active acidic surface of the cation-exchange resin as similarly revealed in a related investigation [15].

Catalyst	**Some Surface Properties of the Resins Catalysts**				
	Form	**Moisture (%)**	**Surface area (m2/g)**	**Pore Size (mL/g)**	**Particle Size (mm)**
Amberlyst-A26	Beads	66-75	30	0.30	0.560-0.700
Amberlyst-36	Beads	51-57	33	0.20	0.425

Table 1:- Physicochemical Properties

Therefore, the week active acidic site of Amberlyst-36 catalyst and relatively smaller pores has offered limited accessibility to triglyceride molecule with a resultant lower performance despite good physical properties of the material. Consequently, in the subsequent studies, influences of temperature, catalyst loading as well as catalyst stability and reuse as factors or parameters that influences biodiesel production was investigated and optimised on Amberlyst-A26 been the most promising and active system only.

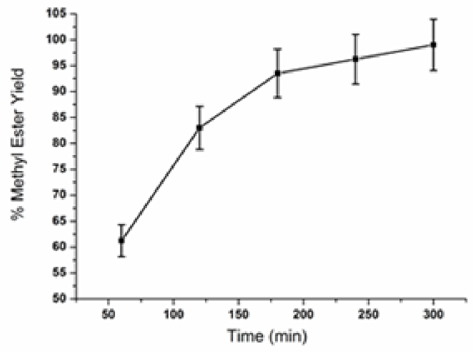

Fig. 2 progress of biodiesel synthesis over time, the figure shows how methyl ester yield changes with time which signifies importance of reaction time in biodiesel synthesis

B. Triglyceride Conversion Over Time to Biodiesel

Relationship between triglyceride conversion to methyl ester (biodiesel) and the period (time) of transesterification reaction was investigated using reaction condition of 1g of Amberlyst-A26 catalyst and most suitable vegetable to oil ratio of 1:60 at 60 °C. Samples were taken hourly and analysed using ^{1}H NMR after dissolution in deuterated chloroform. The result shown in Figure 2 suggests that triglyceride conversion to methyl ester changes linearly with time of reaction until maximum yield or equilibrium was attained. Highest biodiesel yield of 99% was recorded in five hours which depicts the optimised reaction time in this work. Essentially, the result shows that highest and maximum triglyceride conversion to biodiesel of 99% was attained within five hours of the test. Nonetheless, a very good yield >60% was attained within one hour of the test and a yield >80% within two hours respectively. After two hours, not much increase in the conversion or biodiesel yield was observed thereafter. This suggests maximum triglyceride conversion to biodiesel and highest level of performance of the catalyst occurred within the first three hours of the test. The results further revealed the importance of reaction time to the transesterification of vegetable oil to biodiesel. Attainment of 80% conversion within two hours further corroborates the robust activity of this catalyst as seen in section 3.1 and 3.2 above. The activity of this catalyst can be compared to the performance of homogeneous catalysts with even more advantage because of the integrity of the process being a heterogeneous catalyst that is recoverable and reusable [29,30]. The catalyst has also demonstrated greater activity and stability compared to many ceramic-based heterogeneous catalysts [31,32].

Therefore, polymeric ion exchange resins have robust catalytic behaviour comparable to ceramic-based catalysts and homogeneous catalyst.

C. Optimisation of catalyst amount

Amount catalyst used for the transesterification reaction is also another factor that influences the triglyceride conversion to methyl ester and was optimised in this work. Amberlyst-A26 anion-exchange resin and soybean oil was used for the test. Transesterification of vegetable at 60 °C for five hours using oil to methanol ratio of 1:60 was explored in the study. Catalyst amount in the range of 0.25g-1g was adopted for the investigation. The diagram in Figure 2 shows there is a linear relationship between the triglyceride conversion to methyl ester and the amount or quantity of catalyst used for the test. As the amount changes from 0.25g to 1g, the biodiesel yield also increases to a maximum yield of 99% at 1g. The steady increase is attributable to absence of side reactions such saponification reaction that could slow and reduce biodiesel yield over time compared to when homogeneous catalysts are used [29,33].

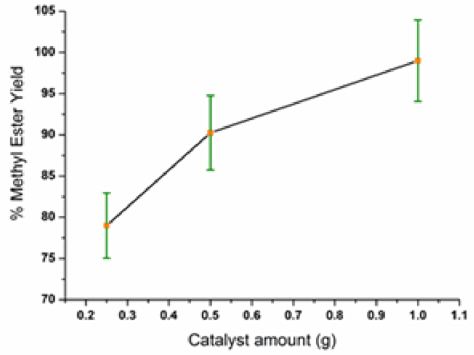

Figure 3 showing the significance of catalyst amount on the biodiesel yield

It is interesting to observe that 0.25g catalyst loading yielded biodiesel >80% and doubling catalyst loading to 0.5g yielded only 15% increase in biodiesel production equivalent to 95% yield so also when increased to 1g only 4% i.e. 99% difference in yield was recorded. These attest to the robust catalytic behaviour of the resin catalyst. The trend in conversion revealed that further increase in the catalyst amount beyond 1g might lead to decline in conversion. The results suggest that that small catalyst loading of 0.25g is capable of yielding remarkable product. The observed trend could be attributed to the use of reasonable and suitable catalyst amount as excess of it could lead to poor contact and difficulty in catalyst active site accessibility and resultant low yield as reported in related study [31,32]. More so, in transesterification reaction to biodiesel, one of the limiting factors that delayed conversion and biodiesel yield is the vegetable oil-catalyst-methanol triple phase intermediate build-up. This is largely reduced by optimisation and careful choice of catalyst loading and reaction parameters that affects biodiesel yield in order to improve miscibility of the reactants and catalyst for maximum triglyceride conversion to methyl ester.

D. Influence of transesterification temperature

The influence of reaction temperature on the vegetable oil conversion to biodiesel was looked at in this study. The reaction temperature was limited to 60 °C using Amberlyst-A26 as shown in Table 1 to prevent catalyst decomposition. Figure 2 shows a linear relationship between the biodiesel production and reaction temperature. Maximum yield >99% was recorded at 55 °C which suggests the optimum reaction temperature. Interestingly, triglyceride transformation to biodiesel >90% was obtained at 40 °C reaction temperature depicting robust catalytic properties, high efficiency and activity of this material.

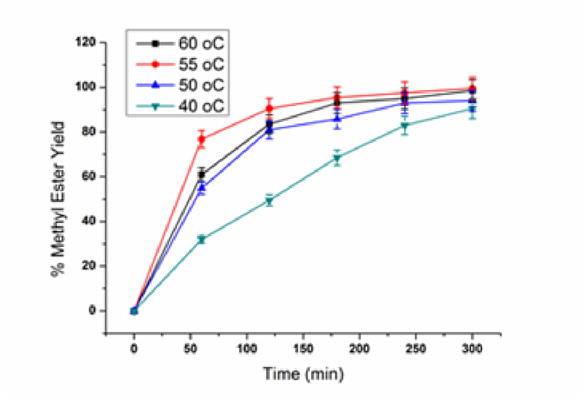

Fig. 4 Influence of reaction Temperature and progress in triglyceride conversion to biodiesel over time

Transesterification reaction performed at low temperatures reduces cost of production and make the process economically viable which is one of the issues of concern in the biodiesel industry. The catalyst activity observed in this test with Amberlyst-A26 being heterogeneous-recoverable and reusable compares with better advantage than very active homogeneous catalyst such as KOH, NaOH [28]. This test further corroborates an earlier observation that the first two hours of the test recorded substantial yield >80%. There was no much increase in yield of biodiesel (about 10% only) after the two hours start up time to five hours of the study which suggests stabilisation of the biodiesel production after few hours. Hence at reaction temperatures of 50-60 °C, two hours represents the optimum time to attain maximum yield using Amberlyst-A26 catalyst. This also further revealed that the rate of the triglyceride conversion to biodiesel demonstrated by the catalyst system Amberlyst-A26 could be likened to using homogenous catalysts [2,3,28].

E. Catalyst stability and reusability

1g of the catalysts system Amberlyst-A26 was subjected to repeated usage in a stability and reusability test using 1:60 vegetable oil to methanol ratio at 60 °C with Sunflower oil to further strengthen its robust catalytic properties. The catalyst was recovered after each run washed and reused and Figure 5 shows the trend of the results obtained. The catalyst showed continuous activity with no evidence for depletion of active sites by leaching during transesterification reaction. Only a drop of 19% in catalytic activity was observed after repeated use for thirteen cycles. Compared to some related work [15], the catalyst system is robust and useful for industrial application in biodiesel synthesis. The behaviour of the catalyst was attributed to the fact the solid and beads nature of the catalyst has made it easy to be removed and relatively not dissolvable in methanol medium in the course of transformation process as such no leaching of active phase has occurred hence steady conversion was recorded. This suggests high reusability and stability and economic value when compared to homogenous catalyst systems [28,34] and very much comparable to many ceramic heterogeneous catalyst systems that have demonstrated good catalytic activity [7,8,29].

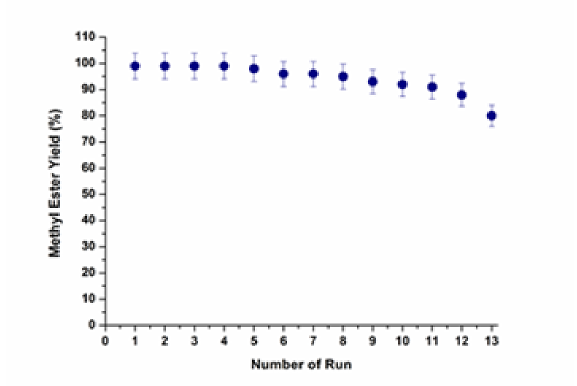

Fig. 5 Catalyst reusability and stability to triglyceride conversion to biodiesel over repeated usage

F. Autoclave Synthesis

In this study, Amberlyst-A26 and Amberlyst-36 catalysts were utilized in transesterification reaction under the severe environment in the autoclave to improve Amberlyst-36 catalytic activity or reduce the vegetable oil-methanol ratio in the case of Amberlyst-A26. Influence of reaction temperature was investigated in the test using 1g catalyst amount and 1:18 vegetable to oil ratio in an oven. In order for the synthesis to be effective, the test was conducted at elevated temperatures above hundred typical of hydrothermal synthesis despite the temperature resistant limitation of the resins-Amberlyst-A26 (60 °C) and Amberlyst-36 (120 °C). Figure 6 shows the trend of the results of the test obtained.

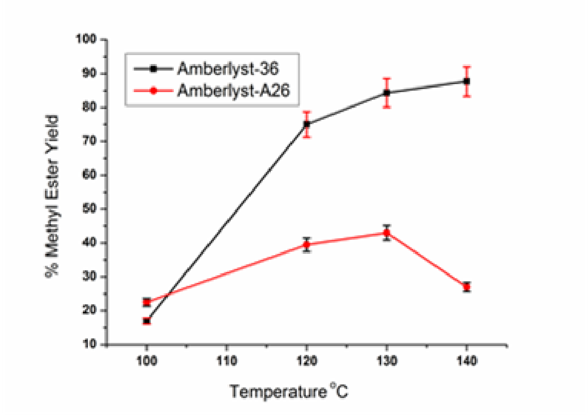

Fig. 6 Influence of temperature on biodiesel yield and progress of conversion over time during autoclave synthesis

The methyl ester production shows a progressive increase on Amberlyst-36 with increase in reaction temperature to a maximum yield of 88% at 140 °C typical of autoclave biodiesel synthesis [25,27] whilst Abmberlyst-A26 gave maximum methyl ester yield of 43% at 130 °C and declined to 26% at 140 °C. In both cases, it is essential to observe that substantial conversion to biodiesel occurred at reaction temperature of 120 °C after which, the conversion began to stabilize. Hence, Amberlyst-36 has shown good stability to high temperature and pressure of the reactor hence yielded better results. The relatively low conversion recorded with Amberlyst-A26 was traced to instability and decomposition of the catalyst under the influence of pressure and temperature in the autoclave. The result demonstrates that Amberlyst-36 has better stability and catalytic activity under stringent condition compared to Amberlyst-A26 that is more active in the conventional test. The results are comparable to the catalytic performance of thermally stable ceramic-based catalyst systems [29].

IV. CONCLUSION

Resin-catalysed transesterification of Sunflower oil to biodiesel was successfully carried out. The porous Amberlyst-A26 basic catalyst with a bigger particle size relatively has demonstrated high catalytic activity even at temperature as low as 40 °C and has shown good stability and reusability compared to the less active and less porous Amberlyst-36 after repeated use. There was no significant evidence of loss or leaching of active phase observed from the use of the Amberlyst-A26 basic ion-exchange resin. Conversely, Amberlyst-36 is more active and selective for biodiesel synthesis under severe transesterification reaction condition of temperature and pressure in autoclave than the Amberlyst-26 whose performance showed decline due to thermal instability and decomposition. Hence, reaction condition could be tailored to enhance performance and reusability of catalyst.

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