Indian Journal of Chemical Technology
Vol. 24, September 2017, pp. 479-487

Leaching of the active component of alumina supported sodium catalysts during the transesterification of soybean oil

Arun Kumar Gupta*[,1,2], Sanjeev Garg[1] & Goutam Deo[1]

[1]Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208 016, India
[2]Department of Chemical Engineering, University Institute of Engineering & Technology
Chhatrapati ShahuJi Maharaj University Kanpur 208 024, India
E-mail: arung247@gmail.com

Received 15 October 2015; accepted 6 April 2017

The transesterification reaction for biodiesel production using soybean oil with several alkali and alkaline metal hydroxides and alkoxides as liquid-phase catalysts has been studied. The hydroxides and alkoxides of sodium (Na) and potassium (K) are found to be the most active. Alumina (Al_2O_3) supported Na is subsequently considered for the synthesis of a suitable solid-phase catalyst. This catalyst was synthesized and characterized. An optimum Na loading of 10 wt% for biodiesel production is determined. This catalyst also show the maximum basicity. The effects of operating conditions for the transesterification reaction using the Al_2O_3 supported Na catalyst are also determined. In all of the reactions involving Al_2O_3 supported Na catalysts leaching of the active component has been observed and the reaction appeared to proceed as a liquid phase catalyzed reaction. The leached amount corresponded to about 20% of the Na present in the Al_2O_3 supported Na catalyst and is independent of the methanol amount. Thus, leaching is a serious consideration for supported Na catalysts.

Keywords: Biodiesel, Soybean, Na/γ-Al_2O_3, Leaching, Transesterification, CO_2 TPD

Biodiesel production from oils of plant origin has been extensively studied[1,2]. These oils are of the edible or non-edible type and contain triglycerides[3]. The chemical transformation of the triglycerides to biodiesel occurs by transesterification. Effective transesterification of triglycerides to biodiesel requires a catalyst[4]. These catalysts are acidic or basic and are present as a liquid or solid phase[5]. Based on the phase of the catalyst, these reactions are usually referred to as homogeneous liquid-phase or heterogeneous solid-phase reactions. In reality, the transesterification of biodiesel with methanol is a heterogeneous reaction since a two phase mixture is formed when triglycerides and methanol are mixed[6].

Amongst the different homogeneous and heterogeneous catalysts studied, the liquid-phase homogeneous base catalysed transesterification reactions were relatively faster[7]. However, these catalysts were also sensitive to the presence of water and free fatty acids, FFA[8]. Furthermore, homogeneous liquid-phase catalysts are usually present in the reaction mixture. To overcome some of the disadvantages of the liquid-phase homogeneous base catalysts, several solid-phase heterogeneous catalysts have been considered[7,9-12]. Some of the solid-phase heterogeneous catalysts contain K and Na supported on a suitable carrier, such as Al_2O_3. The transesterification reaction was then studied using these supported catalysts to understand the effect of various factors. Some of these factors are common with the liquid-phase catalysed reaction, such as methanol to oil ratio, catalyst amount, agitation speed and temperature[7,13], and the other factors are those that are important for solid-phase catalysed reactions, such as catalyst composition and the presence of mass transfer limitations[9].

One of the main considerations for using solid-phase heterogeneous catalyst is their reusability. Reusability is commonly associated with leaching and other forms of deactivation. Leaching effects have not been properly addressed for solid-phase heterogeneous catalysts containing Na[14]. Usually the effect of leaching is examined by checking for active species in the liquid phase after the reaction or reusing the catalyst several times. A suggested method is to mix the solid catalyst with the solvent or liquid phase medium, filter the solid catalyst, and then conduct the liquid phase reaction using the filtrate[15,16]. Any leached species from the solid catalyst will be retained in the liquid phase medium and can facilitate the reaction. Thus, if leaching has occurred then even without the solid phase catalyst the reaction will still proceed with the leached species. Furthermore, reuse of the catalyst after filtering would also give rise to a lower catalytic activity if leaching has occurred. However, the former method is more suitable to study leaching effects though analyses of leaching by both methods are advisable.

Alumina supported Na and K catalysts have been used for biodiesel production from vegetable oils or triolein with satisfactory results[7,9,17]. However, in these studies the leaching of the active component was not considered in detail. For example, in none of these studies, reuse of the supported catalyst was considered. Studies dealing with the use of mixed metal oxide systems containing magnesium and aluminium (Mg-Al hydrotalcites and layered double hydroxides) as solid-phase base catalysts for biodiesel production revealed leaching plays an important role in the production of biodiesel[18,19]. In these studies Na or K were used during the precipitation of the mixed metal oxide phase and were retained in the structure. During biodiesel production using these mixed metal oxide catalysts Na or K phase leached to the liquid phase and was primarily responsible for the reaction. For the Al_2O_3 supported K catalyst a careful study concluded that leaching of the active component occurred[20]. However, studies on the leaching of the active component from Al_2O_3 supported Na catalysts appear to be missing. Thus, it would be appropriate to study the Al_2O_3 supported Na catalysts as a function of various factors relevant to heterogeneous solid phase catalysts for biodiesel production and compare them with the values in the literature. While doing so the effect of leaching will be given special attention.

In the present study, efforts were made to study supported solid-phase base catalyst for biodiesel production. Based on initial results and the observations above Al_2O_3 supported Na catalysts were considered in more detail. These Al_2O_3 supported Na catalysts were characterized for their surface area and by X-ray diffraction (XRD), ultra-violet and visible (UV-vis) spectroscopy and CO_2 desorption studies. The catalysts were then tested for the transesterification of soybean oil. Soybean oil was chosen for this study since it is of plant origin, contains only small amounts of free fatty acids, and is an ideal feedstock for simulation studies. The factors considered for biodiesel production using Al_2O_3 supported Na catalysts were: catalyst composition, methanol to oil ratio, catalyst amount, agitation speed, temperature and leaching.

Experimental Section

Unsupported base catalyst

Sodium, K, calcium (Ca) and magnesium (Mg) methoxides (Sigma-Aldrich) were tested for the transesterification reaction. Commercially available soybean oil was used for biodiesel production.

Supported Na catalyst preparation

Several supported Na catalysts were prepared by the incipient wetness impregnation (IWI) method using Al_2O_3 and silica (SiO_2) as possible support materials. Prior to catalyst preparation the Al_2O_3 (Puralox, SBa 200) and SiO_2 (Aerosil-200) supports were pretreated. The pretreatment of the support was achieved by using previously established procedures[21]. Sodium hydroxide (NaOH, Sigma Aldrich, 99.99%) was used as the precursor for Na. Previous studies have also used NaOH solution as a precursor for synthesizing Al_2O_3 supported Na catalysts[7,17]. The pre-treated support was impregnated with calculated amounts of NaOH solution of incipient wetness volumes. Following impregnation and drying, a pre-defined temperature ramp was used and the supported catalysts were finally calcined at 773 K for 6 h. The catalysts were prepared by calculated amount of precursor to form Al_2O_3 supported Na catalysts of different loadings corresponding to: 2, 5, 10, 15, 20 and 30 wt%. It was assumed that the amount of Na taken in the precursor solution was the same amount incorporated in the Al_2O_3 supported Na catalysts. These catalysts were referred to as: xNa/Al_2O_3 and xNa/SiO_2, where x is the weight percent of Na. The SiO_2 support was relatively difficult to process while synthesizing the silica supported catalyst and considering that the biodiesel yields were similar for the two supported systems, further studies were restricted to Al_2O_3 supported Na catalysts.

Catalyst characterization

The surface area of the catalyst samples were measured using nitrogen adsorption at 77 K in a SMART SORBS 92/93 set up. The single point BET equation was used to calculate the surface area. The XRD patterns of the supported samples were obtained with a 180 Debye Flex-2002 X-ray diffractometer. Nickel filtered K_α radiation of a copper target (λ=1.541841 A^o) was employed, and the data was obtained from 20° to 70° in a step mode at a 2θ sweep of 3° min^{-1} and a time constant of 3.0 s. The UV-vis spectra were obtained using a Cary 5000 UV-vis-NIR spectrophotometer equipped with a Harrick Scientific diffuse reflectance accessory. All spectra were collected under ambient conditions with $BaSO_4$ as the reference[22].

The basicity of the Na/Al_2O_3 catalyst was determined by temperature programmed desorption (TPD) of CO_2 using AMI-200 (Altamira Instruments). The CO_2 TPD analysis was performed in U-tube, packed bed of different catalyst loading. The whole analysis was conducted in several steps. About 100 mg of sample was initially treated with Argon (Ar) gas from 303 K to 623 K at the rate of 10 K/min and kept at 623 K for 1 h. The sample was then cool to 323 K at a rate of 10 K/min. In the second step the sample was treated with diluted CO_2 gas (10% CO_2 in Ar) flowing at a rate of 50 mL/min at 323 K for 0.5 h. The sample was then flushed with Ar at 323 K for 0.5 h to remove excess CO_2. Finally, the sample was heated from 323 to 823 K at the rate of 10 K/min using Ar as the carrier gas. The desorbed amount of CO_2 was calculated by pulse calibration of a 10% CO_2-Ar mixture.

Reactor used

A 2.0 litre batch reactor (AmAr Equipments Ltd, Mumbai, India) was used for most of the transesterification experiments. The reactor was equipped with a PID controller, a RTD-PT100 temperature sensor, an electrically heated jacket, a condenser with a cooling water circulation system, an agitator for proper mixing, a valve for sample removal and gauges. The same batch reactor was previously used for biodiesel production[23]. Bench top experiments were also performed in an agitated 250 mL beaker with proper temperature control. The bench top experiments were performed for exploratory studies.

Experimental procedure

Measured amounts of methanol and 1.5% g/g-oil liquid-phase catalysts[24], were thoroughly mixed at room temperature. This solution was then added to the bottom of the batch reactor or beaker depending on the type of study. In the beaker experiments, 100 g of soybean oil was added and the temperature was then raised to 333 K. The reaction was allowed to proceed for 1 h after which the biodiesel yield was determined. In the 2 litre batch reactor experiments, 250 g of soybean oil was added and then the transesterification reaction using solid-phase catalysts were carried out from 293 K to 333 K. At each temperature, a fresh stock of reactant and solid catalyst was considered. The required amount of supported catalyst and volume of methanol, with methanol to oil molar ratios of 3:1, 6:1, 12:1 or 24:1, were added to the reactor. To calculate the molar ratio, the molecular weight of soybean oil was taken to be 882.82 g/mole. A previous study reported a molecular weight of soybean oil as 874 g/mole[25]. Samples (about 20 mL) were withdrawn at various time-intervals for biodiesel yield determination. The withdrawn samples were allowed to settle for 12 h, which was followed by mild shaking and washing of the upper biodiesel containing layer with distilled water that was at 343 K. The upper ester layer of the samples were analysed with ^1H NMR spectroscopy for the calculation of yield using previously established procedures[26]. Several runs were repeated to check for reproducibility and the average value was reported. The variations of biodiesel yields were less than 5%.

Catalyst leaching

To study the effect of catalyst leaching, the following procedure was followed. The powder form of an Al_2O_3 supported Na catalyst was mixed with the amount of methanol required for the reaction. The amount of methanol required was according to the methanol to oil ratio. The solid-phase was then separated from the liquid phase by decantation and then by filtration. The liquid phase containing methanol and any leached material was then taken in the beaker or batch reactor specified above. A known amount of oil corresponding to the methanol to oil was then mixed with the liquid phase mixture and the reaction was carried out under the appropriate operating conditions based on the specific study.

Results and Discussion

The performance of different unsupported base catalysts were tested in a 250 mL agitated beaker operating at 333 K and the yields were determined after 1 h of reaction. The transesterification reaction was performed with 100 g of soybean oil with catalyst concentration of 1.5 wt% and methanol to oil ratio of 6:1. The Na and K methoxide samples were readily soluble in methanol, however, Ca and Mg methoxides still appeared as suspensions in the methanol phase. Comparing the different unsupported base catalysts, it was observed that Na methoxide and K methoxide showed a high biodiesel yield of 80 to 100%. In

Table 1 — The biodiesel yield, surface area and amount CO_2 desorbed of the different Na/Al_2O_3 catalysts

Sample	Na/Al_2O_3 (% loading)	Biodiesel yield* (%)	Surface area (m^2/g)	CO_2 desorbed (μmol/g-cat.)
Al_2O_3	0	0	145	480
2 Na/Al_2O_3	2	0	137	480
5 Na/Al_2O_3	5	17	110	590
10 Na/Al_2O_3	10	39	86	590
15 Na/Al_2O_3	15	19	32	290
20 Na/Al_2O_3	20	4	12	300
30 Na/Al_2O_3	30	3	3	80

*Reaction conditions: Time = 1 h; T = 333 K; rpm = 750; oil = 100 g; methanol:oil = 6:1.

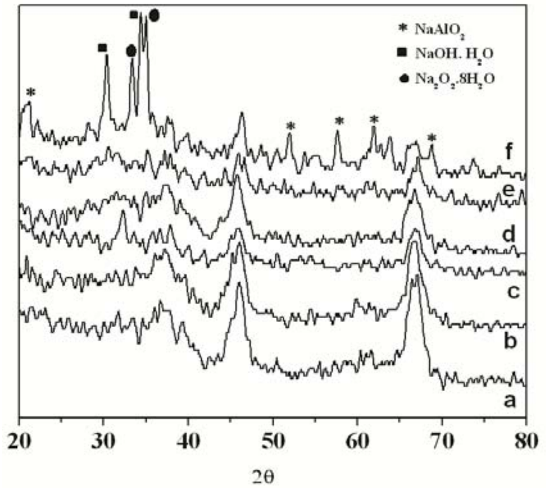

Fig. 1 — X-ray diffraction patterns for the Al_2O_3 supported Na samples.
(a) $2Na/Al_2O_3$; (b) $5Na/Al_2O_3$; (c) $10Na/Al_2O_3$; (d) $15Na/Al_2O_3$; (e) $20Na/Al_2O_3$; (f) $30Na/Al_2O_3$.

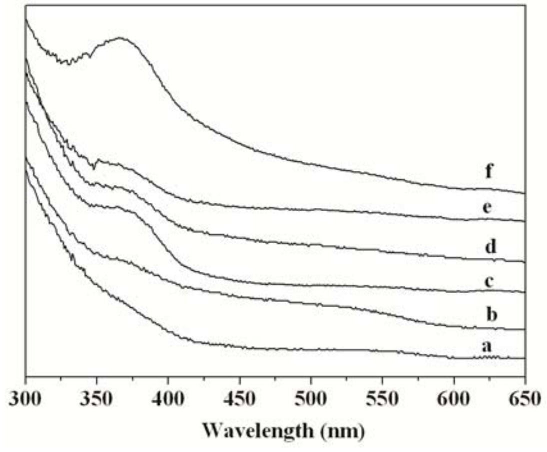

Fig. 2 — UV-vis spectra of the Al_2O_3 supported Na samples.
(a) $2Na/Al_2O_3$; (b) $5Na/Al_2O_3$; (c) $10Na/Al_2O_3$; (d) $15Na/Al_2O_3$; (e) $20Na/Al_2O_3$; (f) $30Na/Al_2O_3$.

contrast, Camethoxide showed a low biodiesel yield of 15 to 20%, and Mg methoxide showed no biodiesel yield under the present experimental conditions. Thus, Na and K were considered as likely candidates for synthesizing supported catalysts. Furthermore, considering the availability and previous studies on leaching of supported K catalyst[20], Al_2O_3 supported Na catalysts were synthesized, characterized and tested for the transesterification of soybean.

The different Al_2O_3 supported Na catalysts synthesized were characterized by determining their surface area, obtaining their XRD patterns and UV-vis spectra, and determining their CO_2 desorption amounts. The surface area of the supported Na samples synthesized were determined and presented in Table 1. The surface area of the supported samples monotonically decreased as the Na loading increased. This was expected since with an increase in loading, there is a possibility of pore blockage. The XRD patterns of the Na/Al_2O_3 catalysts are shown in Fig. 1 and were similar to those previously observed[7]. The $2Na/Al_2O_3$ and $5Na/Al_2O_3$ samples revealed patterns of the Al_2O_3 support. The absences of new peaks suggest that the Al_2O_3 support was essentially unaffected during synthesis. For the $10Na/Al_2O_3$ sample new features were observed and these features gradually become more intense when the Na loading was increased. These additional features were due to the oxides and hydroxides of Na in the hydrated forms. The formation of Na aluminates was evident in the XRD pattern of the $30Na/Al_2O_3$ sample. The UV-vis spectra of the supported catalysts were also obtained and shown in Fig. 2. Figure 2 revealed the presence of a band at about 370 nm for 10% and higher loadings of Na. A similar band was observed for Na aluminate solutions of high alkali concentration and was associated with an Al_2O_3 species of high coordination number[27].

The amounts of CO_2 desorbed from the different supported Na samples were determined from the TPD experiments and tabulated in Table 1. The amount of CO_2 desorbed increased with Na loading up to

$10Na/Al_2O_3$, and then decreased when the loading was further increased. The amount of CO_2 desorbed is indicative of the basicity of the catalyst[28,29] and the results reveal that the Al_2O_3 supported Na catalysts possess surface basic sites that increase and then decrease as the Na loading is increased. It appears that the increase in surface basic sites was due to the availability of the majority of Na deposited and the decrease was due to the unavailability of all the Na for CO_2 adsorption. A part of the Na is also lost in the formation of compounds, such as aluminates, as observed from the XRD studies.

The effect of Na loading and amount of catalyst were initially determined using agitated beaker experiments. The results showing the effect of Na loading on the biodiesel yield are presented in the third column of Table 1. It was observed that the biodiesel yield initially increased and then decreased when the Na loading was increased. Specifically, the $10Na/Al_2O_3$ sample provided the highest biodiesel yield. It would appear that the relative basicity of the solid-phase catalyst plays an important role since the trend in biodiesel yield with Na loading was similar to the relative basicity of the Al_2O_3 supported Na catalysts. Such a correlation between the basicity and the biodiesel yield has been previously suggested[17].

Comparing the biodiesel yields of liquid-phase catalysts mentioned above with those of supported catalysts given in Table 1 revealed that the Al_2O_3 supported Na catalysts produced less biodiesel than the equivalent amount of NaOH liquid phase catalyst. Such differences were attributed to mass transfer effects or the limited availability of surface sites[7,30]. Furthermore, the results showing the effect of the amount of the $10Na/Al_2O_3$ catalyst to be used with 100 g oil revealed that the biodiesel yield increased when the amount of the catalyst was increased up to 3.5 g. A further increasing in the amount of catalyst resulted in a more gradual increase in the biodiesel yield. Considering the above observations, 3.5 g of $10Na/Al_2O_3$ per 100 g of oil was considered for further investigation.

Effect of agitation speed

To study the effect of agitation speed, experiments were performed with a 6:1 methanol to oil ratio, a temperature of 313 K and four agitation speeds, namely, 100, 250, 500 and 750 rpm. The results of these experiments are shown in Fig. 3. The biodiesel yields using a liquid-phase catalyst containing 3.75 g Na in 250 g soybean oil with an agitation speed of 250 rpm are also included. The results reveal that for the solid-phase supported catalyst the reaction rates are similar for 250 to 750 rpm agitation speeds. Furthermore, the biodiesel yield for the 250 to 750 rpm agitation speed approached a constant value of about 65%. The biodiesel yield for 100 rpm agitation speed was lower, and appeared to approach the biodiesel yield value of 65%. Soybean oil and methanol are essentially immiscible and agitation speed plays an important role in improving mass transfer between the phases[31]. The presence of a solid catalyst provides an extra mass transfer step. Thus, determining appropriate agitation speeds are crucial[32]. The present study reveals that an agitation speed of at least 250 rpm is required to minimize mass transfer effects. A previous study suggested that for agitation speeds of 300 rpm and higher does not affect the final biodiesel yield[17]. However, the time evolution of biodiesel yields shown in the present study was not given in that previous study.

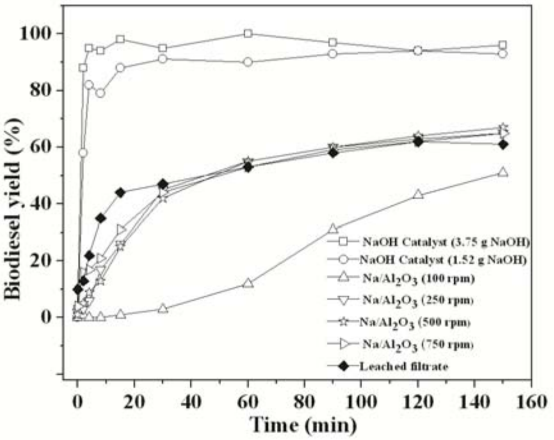

Fig. 3 — The effect of agitation speed on the transesterification reaction.
Reaction conditions: T = 313 K; oil = 250 g; catalyst wt. ($10 Na/Al_2O_3$) = 3.5 g/100 g oil; methanol: oil = 6:1.
The transesterification reaction using liquid phase catalyst/leached catalyst.
Reaction conditions: T = 313 K; rpm = 250; oil = 250 g; catalyst =NaOH; methanol:oil = 6:1.

Comparing the transesterification reaction using liquid phase catalysts containing 3.75 g of Na with the Al_2O_3 supported Na catalyst revealed that when a liquid phase catalyst was used, the biodiesel yield rapidly approached about 95%. In contrast, the reaction rates of the transesterification reaction using solid the Na/Al_2O_3 catalysts were slower and approached a lower biodiesel yield of 65%. A slower initial reaction rate and lower biodiesel yield was also previously observed[7].

To further investigate the slower reaction rates and lower biodiesel yields observed over the supported catalyst, an equivalent amount of Na present in the Al_2O_3 supported Na catalyst was taken, i.e., 1.52 g of sodium hydroxide in 250 g soybean oil, and a liquid phase reaction was performed. The results of the liquid phase are also included in Fig. 3. The biodiesel yields were similar to the homogeneous liquid phase catalyst reaction mixture containing 3.75 g Na. At this point, it would appear that the results shown for the effect of agitation speed in Fig. 3 were indeed an effect of solid phase catalyzed reactions, where the surface sites of the catalyst plays an important role. However, care must be taken to ascertain the effects of leaching of the active component.

Following the procedure suggested for testing the effects of leaching[15,16], the Al_2O_3 supported Na catalyst was dissolved in the amount of methanol used for the reaction and the solid phase was then filtered. The leached filtrate was then mixed with the required amount of soybean oil and the reaction was carried out. The results of this experiment using the leached filtrate were also included in Fig. 3. Interestingly, the results revealed that the experiments showing the effect of agitation speed of the supported Na catalysts were primarily due to the leached Na into the liquid phase reactant mixture since the final biodiesel yields were similar. The differences between the homogeneous reaction using the leached filtrate and the supported Na catalyst at different agitation speeds greater than 100 rpm were only related to the initial rates. The differences in the initial rates may be related to the differences in the rate of leaching that occurs for the Al_2O_3 supported Na catalyst compared to the filtrate solution, which already has the active component leached into the solution.

Using titration, the amount of Na in the leached filtrate was determined to be about 0.18 g, which corresponds to about 20% of Na being leached from the supported catalyst into the filtrate. The remaining Na appears to be strongly bound to the support and unavailable for leaching and also for biodiesel production. Indeed, only a small amount of biodiesel was produced, 3%, when the solid phase of the leached catalyst was reused, suggesting that the remaining Na was unavailable. Furthermore, the XRD patterns and UV-vis spectra of the $10Na/Al_2O_3$ catalyst before and after reaction revealed changes that were consistent with leaching of Na from the catalyst. Comparison of the reaction data of the leached filtrate containing 0.18 g Na with the liquid-phase reaction using 3.75 or 1.52 g NaOH revealed differences in the initial rate of biodiesel production and the final biodiesel yield achieved. Previous studies reveal that the liquid-phase transesterification reaction was affected by the amount of NaOH and an optimum amount of NaOH exists[7,9]. A lower than optimum amount of NaOH used for the liquid phase transesterification reaction gave rise to lower initial rates and smaller biodiesel yields that can be achieved. The trends in initial rates of biodiesel yield and final biodiesel yield achieved for the leached filtrate and liquid-phase transesterification reaction using NaOH observed in the present study were consistent with these previous results. Thus, leaching of 20% of the Na present in the Al_2O_3 supported Na catalyst appears to explain the observations.

Effect of methanol to oil molar ratio

To further address the concerns of leaching, the effect of methanol to oil ratio was also studied. Thermodynamics would suggest that the equilibrium conversion of the transesterification reaction can be shifted towards additional biodiesel production by using methanol in excess. Excess of alcohol is, however, not always desirable since glycerol, the by-product, is soluble in additional methanol[2,33]. The transesterification reaction was performed with a stoichiometry ratio of 3:1 and three other methanol to oil molar ratios that possessed methanol in excess, namely, 6:1, 12:1 and 24:1. Various methanol to oil ratios were also considered in previous studies[7,17]. The results of the present study are shown in Fig. 4. The results in Fig. 4 reveal that with an increase in methanol to oil ratio, the initial reaction rate decreases. The decrease in initial rate with increase in methanol to oil ratio has been attributed to the decrease in the homogeneity of reaction mixture[34]. It should be noted that with an increase in methanol to oil ratio, the concentration of triglycerides, the limiting reactant, also decreases, which may be cause for the decrease in the initial rate. However, the final biodiesel yield for the 6:1, 12:1 and 24:1 methanol to oil ratios reached a similar value of about 65% in 6 h and was different from the final yield achieved with a methanol to oil ratio of 3:1, where a lower biodiesel yield of about 49% was achieved.

The effect of catalyst leaching for some of these experiments was also studied by using the 10Na/Al_2O_3 sample with an appropriate amount of methanol corresponding to a methanol to oil molar ratio of 3:1 and 6:1 to produce the leached filtrate. After filtering, the leached filtrate was used for the reaction and the biodiesel yield achieved after the same reaction time was compared with the biodiesel yield achieved using the 10Na/Al_2O_3 catalyst in the first four rows of Table 2. Intermittent data were not collected for these studies. The first four rows of Table 2 revealed that the biodiesel yields were similar for the reaction using the leached filtrate and the 10Na/Al_2O_3 catalyst. Analysis of the filtrate for both methanol to oil ratio also revealed that about 20% of Na had leached from the solid phase catalyst. Thus, leaching occurred for both methanol to oil ratios and the amount of Na leached appeared to be independent of the amount of methanol used.

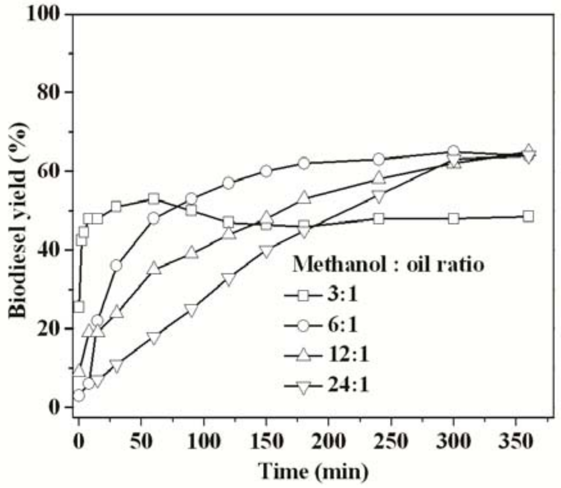

Fig. 4 — The effect of methanol to oil molar ratio on the transesterification reaction. Reaction conditions: T = 313 K; rpm = 750; oil = 250 g; catalyst wt. (10 Na/Al_2O_3) = 3.5 g/100 g oil.

Effect of reaction temperature

Finally, the effect of reaction temperature on the biodiesel yield for a methanol to oil ratio of 6:1 was studied and the results are shown in Fig. 5. The experiments were performed at 293, 303, 313, 323 and 333 K. The initial reaction rate increased with reaction temperature up to 313 K. Similar results were observed previously for liquid-phase homogeneous catalysts[13]. At about 2 h and above the biodiesel yields appeared to approach a constant value, which was different for each reaction temperature. The constant biodiesel yield values increased with reaction temperature; from 30% at 293 K, to 52% at 303 K and to 65% at 313 K. For 313 K and 323 K, the initial biodiesel yield values were similar, However, the final yields were different. At 333 K, the biodiesel yields were slightly higher; however, the final biodiesel yields for 323 K and 333 K were similar, 73%.

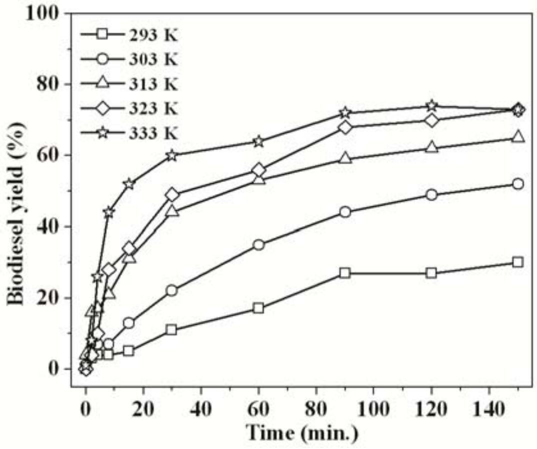

Fig. 5 — The effect of reaction temperature on the transesterification reaction.
Reaction conditions: rpm = 750; oil = 250 g; catalyst wt. (10 Na/Al_2O_3) = 3.5 g/100 g oil; methanol: oil = 6:1.

Table 2 — Comparison of biodiesel yield using Al_2O_3 supported Na catalyst and leached filtrate for different methanol to oil ratios and different temperatures

Sample	Methanol:oil ratio	Temperature (K)	Biodiesel yield (%)
10Na/Al_2O_3	3:1	313	49
Leached filtrate of above	3:1	313	55
10Na/Al_2O_3	6:1	313	64
Leached filtrate of above	6:1	313	61
10Na/Al_2O_3	6:1	303	52
Leached filtrate of above	6:1	303	53
10Na/Al_2O_3	6:1	323	73
Leached filtrate of above	6:1	323	65

Reaction conditions: rpm = 750; oil = 250 g; catalyst wt (10Na/Al_2O_3) = 3.5 g/100 g oil. Time = 4 h.

Using the filtrate based on a methanol to oil ratio of 6:1 the effect of temperature on the biodiesel yield was also studied and the results were compared with the yields achieved using the solid supported catalyst. The biodiesel yields at 303, 313 and 323 K were only considered in these studies. Comparisons of the biodiesel yields achieved using the Al_2O_3 supported Na catalyst and leached filtrate are also shown in the last six columns of Table 2. Again there was a close correspondence between the biodiesel yields achieved using a solid phase supported catalyst and the liquid phase catalyst using the filtrate solution reiterating that leaching occurs at all operating conditions considered.

Thus, the present study revealed that the transesterification reaction of soybean oil using Al_2O_3 supported Na catalysts was primarily, if not entirely, due to the homogeneous liquid-phase base catalyzed reaction. Previous studies have also highlighted the effect of leaching without specific mention about Al_2O_3 supported Na catalysts[20,35]. The present study also revealed that though the characterization of the catalyst suggests that catalysts of different basicity were formed, these characterization results were inconsequential since they have been done at conditions that were not directly relevant for the specific reaction where the catalyst was used. The active sites were present in the liquid phase and not on the solid phase supported system. Finally, it is imperative that while studying solid-phase heterogeneous catalysts for biodiesel synthesis the effect of leaching needs to be considered while developing a suitable solid phase catalyst for biodiesel production.

Conclusion

Based on results from liquid-phase catalysts, a series of Al_2O_3 supported Na catalysts have been synthesized, characterized and tested for the transesterification of soybean oil to bio-diesel. Characterization studies using CO_2 desorption reveal that there is an optimum loading of Na in the solid-phase Al_2O_3 supported catalyst that possessed the highest basicity. This catalyst contain 10 wt % Na and give the highest biodiesel yield. However, leaching of Na from the Al_2O_3 supported catalyst occur while studying the effect of different operating conditions. The amount of Na leached is about 20% of the Na present in the supported catalyst, which appear to be independent of the amount of methanol used. The effect of different operating conditions on the biodiesel yield is also rationalized based on the amount of Na leached. Thus, the possibility of effectively using supported alkali catalysts for biodiesel production without leaching occurring appears doubtful.

References

1 Srivastava A & Prasad R, *Renew Sustainable Energy Rev*, 4 (2000) 111.
2 Meher L C, Sagar D V & Naik S N, *Renew Sustainable Energy Rev*, 10 (2006) 248.
3 Schuchardt U, Serchelt R & Vargas R M, *J Braz Chem Soc*, 9 (1) (1998) 199.
4 Karmee S K & Chadha A, *Bioresour Technol*, 96 (2005) 1425.
5 Pinto A C, Guarieiro L L N, Rezende M J C, Ribeiro N M, Torres E A, Lopes W A,Pereira PAdP & DeAndrade J B, *J Braz Chem Soc*, 16 (6B) (2005) 1313.
6 Marchetti J M, Miguel V U & Errazu A F, *Renew Sustainable Energy Rev*, 11 (2007) 1300.
7 Arzamendi G, Campo I, Arguinarena E, Sanchez M, Montes M & Gandıa L M, *Chem Eng J*, 134 (2007) 123.
8 Dorado M P, Ballesteros E, Almeida J A, Schellet C, Lohrlein H P & Krause R, *Trans* ASAE, 45(3) (2002) 525.
9 Xie W, Peng H & Chen L,*Appl Catal A*, 300 (2006) 67.
10 Kouzu M, Kasuno T, Tajika M, Yamanaka S & Hidaka J,*Appl Catal A*, 334 (2008) 357.
11 Bournay L, Casanave D, Delfort B, Hillion G & Chodorge J A, *Catal Today*, 106 (2005) 190.
12 Kawashima A, Matsubara K & Honda K, *Bioresour Technol*, 99 (2008) 3439.
13 Noureddini H & Zhu D, *J Am Oil Chem Soc*, 74 (1997) 1457.
14 Serio M D, Tesser R, Casale L, D'Angelo A, Trifuoggi M & Santacesaria E, *Top Catal*, 53 (2010) 811 .
15 Arends I W C E & Sheldon R A, *Appl Catal A*, 212 (2001) 175.
16 Santacesaria E, Vicente G M, Serio M D & Tesser R, *Catal Today*, 195 (2012) 2.
17 Kim H J, Kang B S, Kim M J, Park Y M, Kim D K, Lee J S & Lee K Y, *Catal Today*, 93 (2004) 315.
18 Cross H E & Brown D R, *Commun*, 12 (2010) 243.
19 Fraile J M, García N, Mayoral J A, Pires E & Roldán L, *Appl Catal A*, 364 (2009) 87.
20 Alonso D M, Mariscal R, Moreno-Tost R, Poves M D Z, Granados M Lp, *Catal Commun*, 8 (2007) 2074.
21 Routray K, Reddy K R S K & Deo G, *Appl Catal A*, 265 (2004) 103.
22 Arco M D, Hernandez E, Martin C, Mateos J & Rives V, Studies in Surface Science and Catalysis, *Proceedings, IUPAC Symposium (COPS 11)*,(Characterization of Porous Solids II, Elsevier), 1991.
23 Kumar R, Tiwari P & Garg S, *Fuel*, 104 (2013) 553.
24 Biswanath H, M.Tech Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, 2007.
25 Xie W & Zhao L, *Fuel*, 103 (2013) 1106.
26 Guillen M D & Ruiz A, *Trends Food Sci Technol*, 12 (2001) 328.
27 Shu-hua M A, Shi-li Z & Hong-bin X U Yi Z, *Trans Nonferrous Met Soc China*, 17 (2007) 853.
28 Gorzawski H & Hoelderich W F, *J Mol Catal A: Chem*, 144 (1999) 181.
29 Taufiq-Yap Y H, Abdullah N F & Basri M, *Sains Malays*, 40 (6) (2011) 587.

30 Taufiq-Yap Y H, Abdullah N F & Basri M, *Appl Catal B*, 61 (2006) 35.
31 Ma F, Clements L D & Hanna M A, *Bioresour Technol*, 69 (1999) 289.
32 Stamenkovic O S, Lazic M L, Todorovic Z B, Veljkovic V B & SkalaD U, *Bioresour Technol*, 98 (2007) 2688.
33 Tomasevic A V & Marinkovic S S, *Fuel Process Technol*, 81 (2003) 1.
34 Tsuji T, Kubo M, Shibasaki-Kitakawa N & Yonemoto T, *Energy Fuels*, 23 (2009) 6163.
35 Ramos M J, Casas A, Rodrı´guez L, Romero R & Perez A, *Appl Catal A*, 346 (2008) 79.