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Final Report on LDRD Project: Biodiesel Production from Vegetable Oils Using Slit-Channel Reactors

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Final Report on LDRD Project: Biodiesel Production from Vegetable Oils Using Slit-Channel Reactors

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Abstract

This report documents work done for a late-start LDRD project, which was carried out during the last quarter of FY07. The objective of this project was to experimentally explore the feasibility of converting vegetable (e.g., soybean) oils to biodiesel by employing slit-channel reactors and solid catalysts. We first designed and fabricated several slit-channel reactors with varying channel depths, and employed them to investigate the improved performance of slit-channel reactors over traditional batch reactors using a NaOH liquid catalyst. We then evaluated the effectiveness of several solid catalysts, including CaO, ZnO, MgO, ZrO_2, calcium gluconate, and heteropolyacid or HPA ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$), for catalyzing the soybean oil-to-biodiesel transesterification reaction. We found that the slit-channel reactor performance improves as channel depth decreases, as expected; and the conversion efficiency of a slit-channel reactor is significantly higher when its channel is very shallow. We further confirmed CaO as having the highest catalytic activity among the solid caralysts tested, and we demonstrated for the first time calcium gluconate as a promising solid catalyst for converting soybean oil to biodiesel, based on our preliminary batch-mode conversion experiments.

ACKNOWLEDGMENTS

CONTENTS

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1. INTRODUCTION

Worldwide petroleum-based energy resources are being depleted – onshore crude oil production peaked decades ago but our demands for petroleum are still going up. The United States' continued dependency on imported petroleum, particularly from the Middle East, has become an important national security issue. Competition for global energy supply from emerging economic powers such as China and India has added to the urgency for searching and developing alternative energy sources that help us reduce our dependency on imported oil. Lastly, environmental concerns such as pollution and global climate changes provide further motivation to address the energy challenge that we face today[1,2].

Biofuels, which are fuels derived from biomass such as corn, soybeans, sunflowers, algae, wood chips, etc., are ideally suited for meeting the future energy challenges because they do not add to global climate changes. This is attributed to the fact that plants use CO_2 to grow during the photosynthesis process; consequently, the CO_2 formed during combustion of biofuels is balanced by that absorbed during the annual growth of plants used as the biomass feedstock. Another key advantage of biofuels over other alternative energy sources is that they can be burned (either alone or mixed with petroleum-derived gasoline) in existing internal combustion engines. Moreover, we can utilize current infrastructure such as pipelines, delivery trucks, and fueling stations to transport and distribute biofuels[3].

In the present work, we focused on the production of biodiesel (which is an important biofuel) from vegetable (e.g., soybean) oils. With the conventional technology, vegetable oil mixed with alcohol (e.g., methanol) reacts in large-scale batch reactors and in the presence of an alkaline liquid catalyst (e.g., NaOH or KOH) to form methyl esters or biodiesel and glycerol or glycerine. The transesterification reaction can take up to 12 hours or longer to complete; and at the end of the reaction, it is necessary to use an acid to neutralize the liquid catalyst and to separate biodiesel and glycerol from the product mixture. The catalyst-neutralization and product-separation steps are time-consuming, tedious, and costly. Readers who are interested in more detailed discussions on the technical aspects of biodiesel production by transterification are referred to a recent review provided by Meher et al.[4]. Apart from the increased costs in their separation and recovery after the transesterification reaction, the alkaline catalysts are corrosive to the equipment and will readily react with free fatty acids to form soaps, an undesired by-

product. It is therefore of interest to explore alternative approaches to the production of biodiesel from vegetable oils, which can raise production efficiency and lower production costs.

One important alternative is to use solid catalysts, which do not require neutralization and can be separated and recovered readily after the transesterification reaction is carried out. Several reports have recently appeared in the literature on the production of biodiesel with solid catalysts[5-10]. Some solid metal oxides such as those of zinc, magnesium, tin, etc. are known catalysts for transesterification of vegetable oils to biodiesel. Unfortunately, some of the metal oxide catalysts act according to an alternative homogeneous liquid-phase reaction mechanism with subsequent production of unwanted soaps. Peter et al.[5] investigated the use of solid zinc-arginate precipitated on carriers manufactured from silicium oxides. About 80% ester yield was achieved within 20 minutes. They carried out their experiments at 125°C. Chai et al.[6] used a hetero-polyacid solid catalyst having activity that was not affected by the presence of free fatty acids. A new continuous process utilizing a mixed oxide of zinc and aluminum as catalyst for the production of biodiesel was recently commissioned in France[10]. It was reported that the catalyst section utilizes two fixed bed reactors for the transesterification reaction, which is carried out at an elevated temperature and pressure. It was further reported that the product does not need elaborate cleaning as used in the homogeneous liquid-phase catalysis.

Another key alternative is to employ continuous channel reactors instead of batch reactors in the production of biodiesel from vegetable oils – operating in the continuous production mode can raise production throughput. Moreover, species-diffusion paths can be significantly reduced, particularly when the channel is very shallow, so as to create efficient mixing and thus result in fast reaction. Though very few technical details were given, Oregon State University (OSU) recently issued a news release titled "Tiny Microreactor for Biodiesel Production Could Aid Farmers, Nation", which reports the development of a micro-reactor for manufacturing biodiesel from vegetable oils[11]. This technological development was based on the M.S. thesis work by Al-Dhubabian[12], which was completed almost a year prior to the news release. In Al-Dhubabian's M.S. thesis work, two micro-reactors with channel length of 2.33 cm, channel width of 1.05 cm, and channel depth of 100 ㎜ and 200 ㎜, respectively, were fabricated and used to convert soybean oil to biodiesel. Shortly after OSU's news release, the University of Texas at Arlington also issued a news release titled "Microreactor Process Developed for Biodiesel Refining",

which trumpets the development of a micro-reactor for processing biodiesel fuel[13]. Similar to OSU's news release, very few technical details were given in UT Arlington's news release, which is understandable from the standpoint of protecting intellectual property. Fortunately, a conference paper entitled "Inverse Determination of Kinetic Rate Constants for Transesterfication of Vegetable Oils" was published most recently by the UT Arlington group led by Prof. Brian Dennis, which provides a glimpse into their experimental and modeling efforts[14].

One drawback in using micro-reactors for converting vegetable oils to biodiesel is that even though the oil-to-biodiesel conversion efficiency may be high, the production throughput is low since the length and width of a micro-reactor are limited to a few centimeters or less (due to the limitations of the micro-fabrication technology used to make the micro-channel) as demonstrated by the research group at OSU led by Prof. Goran Jovanovic and that at UT Arlington. Consequently, the total area of surfaces that can serve as sites for carrying out the transesterification reaction is very small. Another drawback with micro-reactors is that because they are made by microfabrication technology, the manufacturing cost is high. To overcome these two drawbacks, in the present work we employed slit-channel reactors instead of micro-reactors; the channel of a slit-channel reactor can be made by simple machining such that its length and width are limited only by the mechanical strength of the material used instead of the fabrication technology. Thus, the total surface area available for carrying out the transesterification reaction in a slit-channel reactor can be several orders of magnitude higher than that in a micro-reactor. Another important advantage using slit-channel reactors over micro-reactors is that manufacturing cost is significantly lower. The easy machining and associated low cost make it possible to employ slit-channel reactors to convert vegetable oils (spent or fresh ones) on small farms, and in homes and restaurants. It should be pointed out, however, that the channel in a slit-channel reactor is deeper than that in a micro-reactor due to limitations in simple machining. This means that for the same residence time the conversion efficiency using a slit-channel will be lower than that with a micro-reactor.

The ultimate goal is to employ slit-channel reactors having a solid catalyst (or catalysts) coated on the channel surfaces so as to eliminate the need for catalyst neutralization and recovery. Due to time and resource constraints, we didn't attempt to reach the ultimate goal in this project.

Instead, in the present work we fabricated four slit-channel reactors with varying channel depths and conducted exploratory experiments that examined the effects of channel depth on percent or fractional conversion of soybean oil to biodiesel and the effectiveness of six different solid catalysts on catalyzing the soybean oil-to-biodiesel transesterification reaction.

This report is organized as follows. In Chapter 2, slit-channel reactor fabrication, biodiesel-production system setup, and percent-conversion quantification are described. In Chapter 3, results from our exploratory experimental studies are presented and discussed. Lastly, in Chapter 4, a summary of the present work is provided along with recommendations on future efforts.

2. SLIT-CHANNEL REACTOR FABRICATION, BIODIESEL-PRODUCTION SYSTEM SETUP, AND CONVERSION QUANTIFICATION

Four slit-channel reactors with channel depths of 1 *mm*, 2 *mm*, 5 *mm*, and 10 *mm*, respectively, were fabricated. All four slit-channel reactors have a channel width of 2 *mm* and a channel length of 15.24 *cm*. The bottom block of the four reactors was made of nylon and the top block of transparent polycarbonate, which made possible to visualize the flows of soybean oil and the methanol/NaOH solution through the channels. As shown in Figures 1 and 2, soybean oil was introduced through the supply port in the bottom nylon block or plate whereas the homogeneous methanol/NaOH solution was introduced through the supply port in the top polycarbonate plate. The product mixture was collected from the outlet port in the bottom plate. As shown in Figure 1, a neoprene gasket was used to separate and at the same time seal the two parallel blocks that form the slit-channel reactor.

A representative biodiesel-production system set up is shown in Figure 3. Here soybean oil and methanol/NaOH solution were supplied to the slit-channel reactor via two Pulsatron (E-Plus Series) precision pumps manufactured by Pulsafeeder (Punta Gorda, FL). The slit-reactor was heated using a VWR Shaker Bath (Model 1217) manufactured by VMR International.
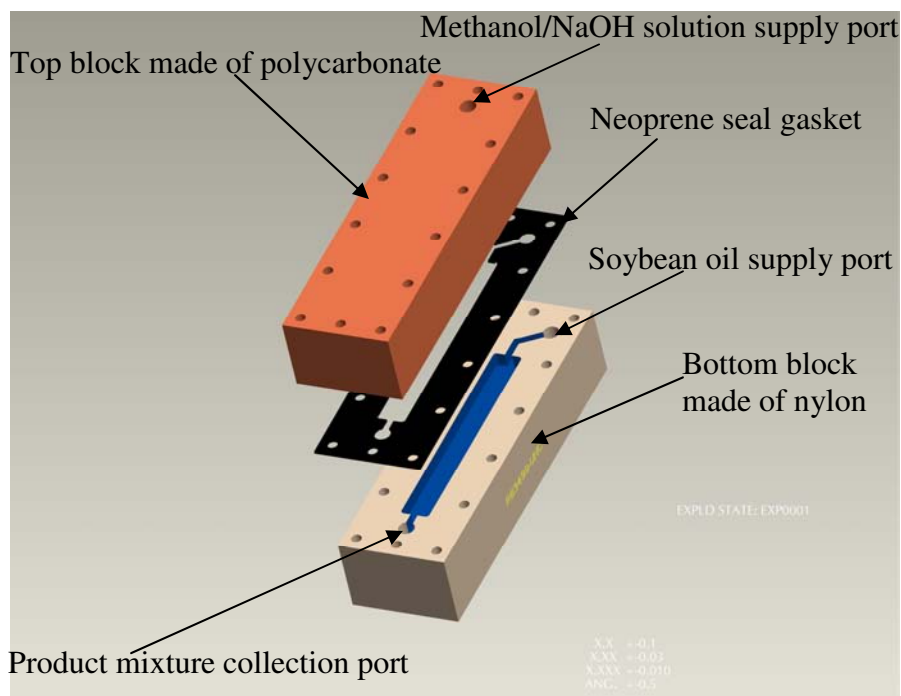
Figure 1: An unassembled slit-channel reactor

Soybean oil supply tubing   Product mixture collection tubing

Top polycarbonate block   Methanol/NaOH solution supply tubing

Figure 2: An assembled slit-channel reactor

Methanol/NaOH supply pump   Soybean oil supply pump

Biodiesel product

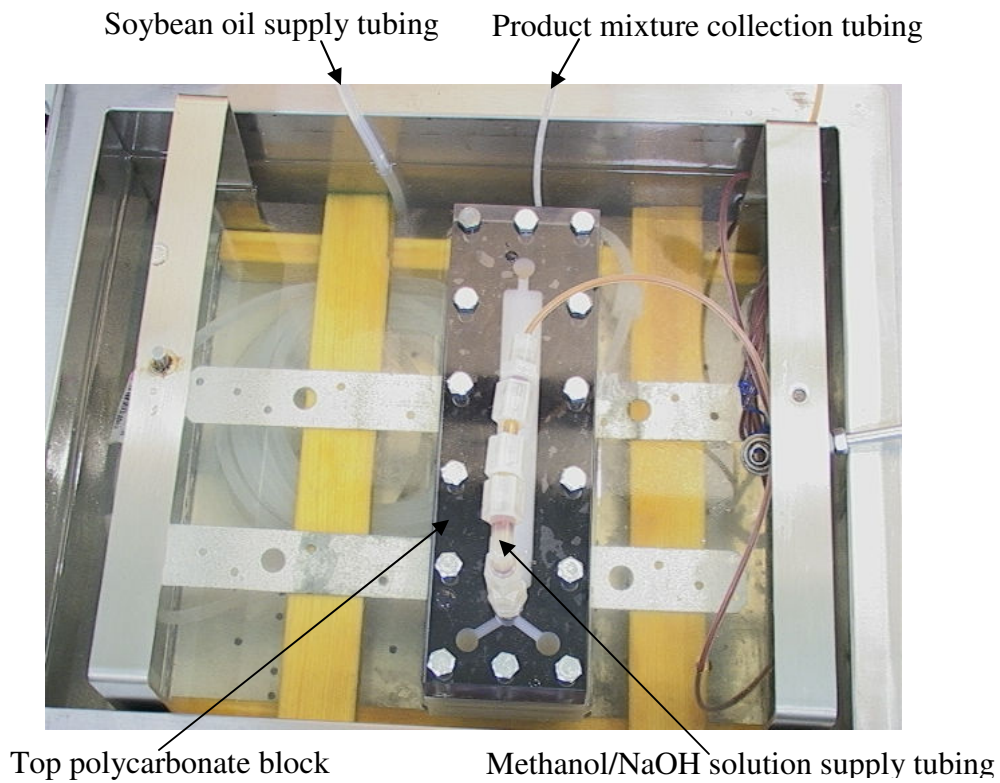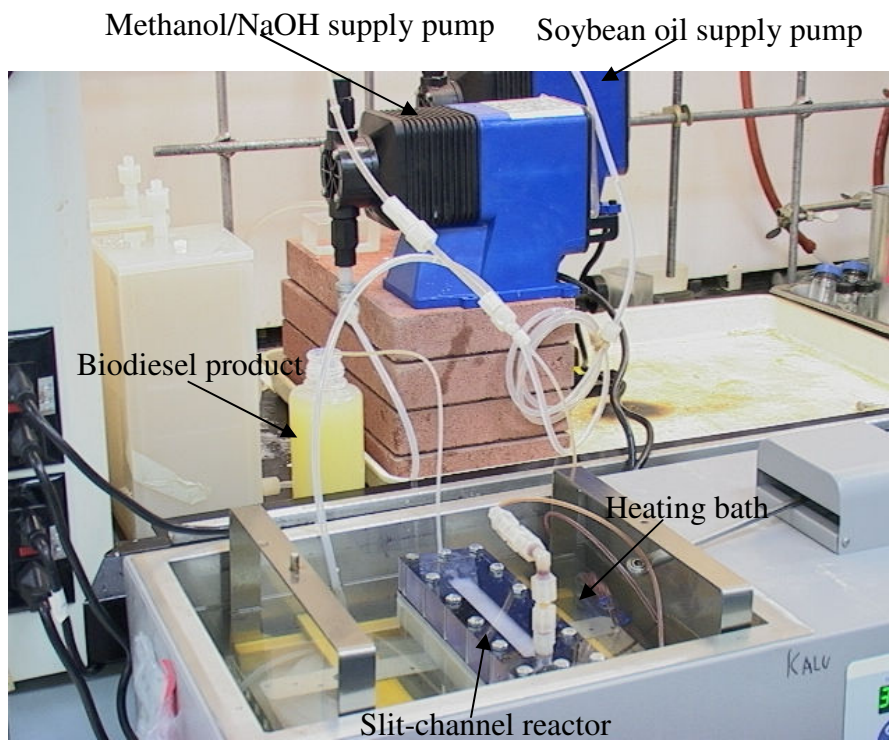Heating bath

Slit-channel reactor

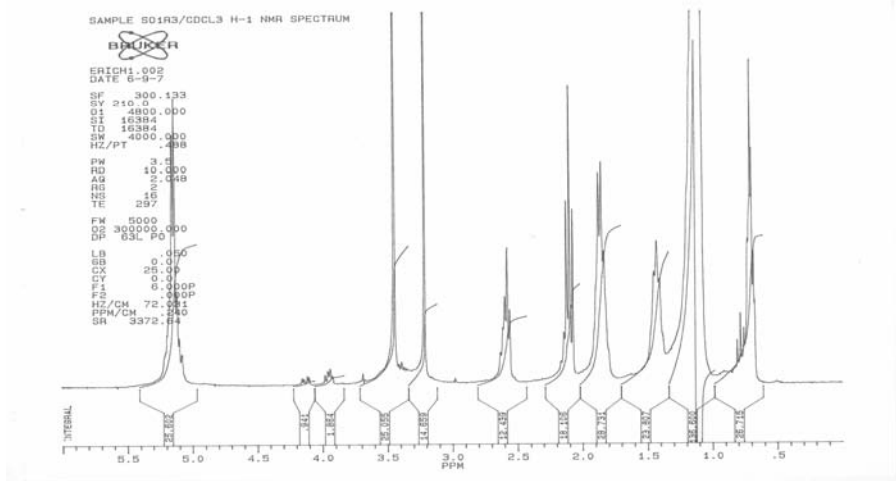Figure 3: Biodiesel-production system setup

Figure 4. Sample ^{1}H NMR spectra

Fractional conversion of soybean oil to biodiesel was quantified using ^{1}H NMR analysis and a Bruker AC300 NMR spectrometer operating at 7.05 Tesla. Pw90 (pulse angle = 90) was 8 μsec with an equilibrium delay of 10 seconds. To calculate the fractional conversion, we followed the approaches of Gelbard et al.[18] and Knothe[19]. Although both methods involve the α-CH$_2$ (methylene) protons in the numerator of the conversion equations, a slight difference exists between the two approaches. Whereas the Gelbard approach involves calculating the ratio of the α-CH$_2$ (methylene) protons adjacent to the triglycerides ester (glyceryl) protons to the methoxy protons of the methyl ester product, Knothe's approach uses the ratio of α-CH$_2$ (methylene) protons to the sum of the methyl ester protons and the glyceryl protons. The chemical shifts of the ^{1}H NMR signals of the α-CH$_2$ (methylene) protons of the soybean oil resonate at δ(^{1}H) = 2.2 – 2.4 ppm whereas the methoxy group of the methyl ester resonate around δ(^{1}H) = 3.5 – 3.7 ppm. Hence, for the Gelbard approach we used Eq. 1 below to calculate the fractional conversion:

$$Fractional\ Conversion = \frac{2I_M}{3I_A} \tag{1}$$

and for Knothe's approach the following formula (Eq. 2) was used:

$$Fractional\ Conversion = \frac{4I_M}{4I_M + 9I_G} \tag{2}$$

where I_M is the integration of the methyl ester protons, I_A is the integration of the methylene protons and I_G is the integration of the glyceryl protons. The numbers used to multiply the integration factors signify the number of protons involved in the group or environment. As an illustration of the approaches, the sample spectra as displayed in Figure 4 shows that at ~ 4.1 ppm, $I_G = 0.941$, at 3.6 ppm, $I_M = 25.055$ and between 2.1 – 2.3 ppm, $I_A = 18.105$. Thus, using Equations 1 and 2 Gelbard's and Knothe's approaches yield 0.923 and 0.922, respectively.

3. RESULTS AND DISCUSSION[*]

3.1 Baseline Performance – Batch Experiments

Several experiments were conducted to verify the appropriate methanol to oil ratio to use, the amount of NaOH catalyst required for ester conversion and the exploration of residence time effects at different reaction temperatures etc. Based on the results of such investigations, some experimental parameter values were chosen. Table 1 summarizes the batch experimental parameters of this work. Several baseline data are qualitative in nature. For instance, the conditions under which the reactor product gels. Such data have not been included in this report.

Table 1: Batch Experimental Parameters

Variable or parameter	Range of values used
NaOH catalyst	0.0263 g/ml of methanol
Temperature	55°C or 60°C or 65°C or room temperature
Methanol:Oil molar ratio	6:1 (equivalent volume ratio 1:4)
Stirring rate	120 -200 rpm

The effect of residence time on the conversion of triglycerides from soybean oil to ester or biodiesel with NaOH liquid catalyst at a temperature of 65°C is shown in Figure 5. The result shows that with NaOH as a catalyst, about 70% triglyceride conversion can be achieved in one hour. The data point at 15 minutes, which shows exceptionally high fractional conversion, is most likely an outlier that was caused by uncertainty in NMR analysis or incorrect methanol to oil ratio being used. Noureddini and Zhu[15] made similar observations with a highly stirred batch system. Other published literature data for well mixed and stirred batch reactors support the results obtained in this work[16]. As has been pointed out in the literature, both temperature of reaction and mixing intensity affect the triglyceride conversion[15]. Thus, the results shown in Figure 5 are unique for the operating conditions employed in the present work.

3.2 Baseline Performance – Slit-Channel Reactors

The motivation for the use of a slit-channel reactor is to obtain improved oil to biodiesel conversion and ultimately develop a solid catalyst that can be utilized in the slit-channel reactor
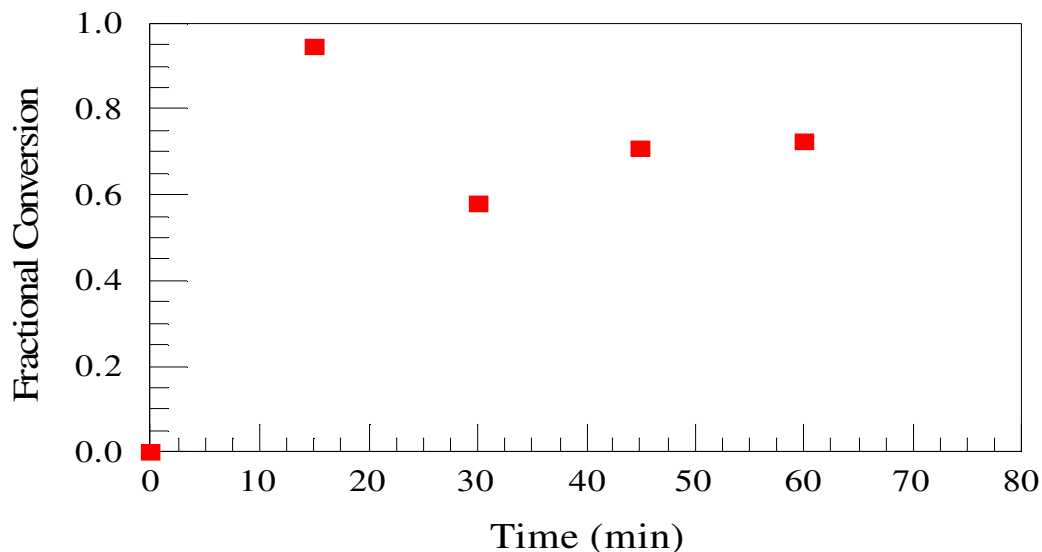
Figure 5. Fractional conversion of soybean oil to biodiesel in a batch reactor
with homogeneous NaOH liquid catalyst at 65 C.

so as to increase production throughput and lower production costs in biodiesel production. In
order to demonstrate the superior performance of slit-channel reactors over batch reactors, NaOH
liquid catalyst was used to obtain fractional conversion data in the slit-channel reactor. In Figure
6, fractional conversion for biodiesel in a 2 mm slit-channel reactor is compared to that in a batch
reactor (which also employed liquid NaOH as catalyst). It is to be noted that the performance (in
terms of fraction conversion) of the slit-channel reactor is dependent on the channel depth as
shown later in this report. Performance of slit-channel reactors with deeper channels approach
that of batch reactors; hence, slit-channel reactors are less efficient than those with shallow
channels. Thus, the fractional conversion improvement shown by the 2 mm channel depth over
the batch reactor supports the core assumption of the present work (which is that a slit-channel
reactor is more efficient in converting soybean oil to biodiesel due to more efficient mixing and
thus faster reaction). Furthermore, the improved performance of the slit-channel reactor is
irrespective of its lower temperature (55° C) of operation over the batch system (65°C). ^{1}H NMR
solution state analysis was used to analyze and determine the conversion of soybean-oil
triglyceride to biodiesel [16-19]. The ratio of the area of the spectra of the methylene protons

15

adjacent to the triglyceride ester group to the area of the spectra of the methoxy protons of the methyl ester product is used for the calculation of the conversion values reported. The details of the ^{1}H NMR method has been provided previously in Chapter 2.
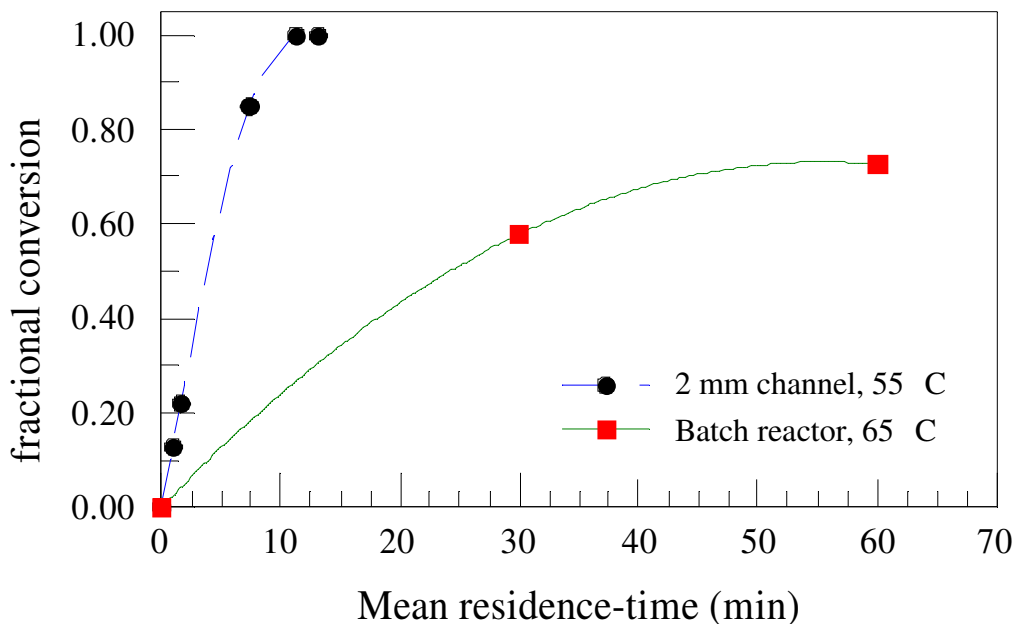
Figure 6. Performance comparison of slit-channel reactor with batch reactor: fractional conversion

3.3 Effect of Channel Depth on Fractional Conversion

The channel depth affects the mode of interaction between reacting species and hence the conversion. It is accepted that a high surface-to-volume ratio, short diffusion distances, fast and efficient heat dissipation and mass transfer enable miniaturized chemical processes to exhibit significant advantages over conventional techniques. Consequently, one would expect the four channel reactors to show individual unique characteristics. In Figure 7, a comparison is made to demonstrate fractional conversion improvement in the slit-channel conversion operation as the channel depth is decreased. As expected, the 1 mm channel shows the greatest improvement. However, the experimental data for the 10 mm and 5 mm channels do not follow the expected trend. The reason for this observation is not clear at this point but could be attributable to several sources of experimental errors including not having exact methanol to oil ratio at all

experimental data points. The importance of the data however should be clear when we compare the 1 mm channel to the 2 mm channel. It is evident in support of the thesis that decreasing the channel depth results in the improvement in conversion efficiency.
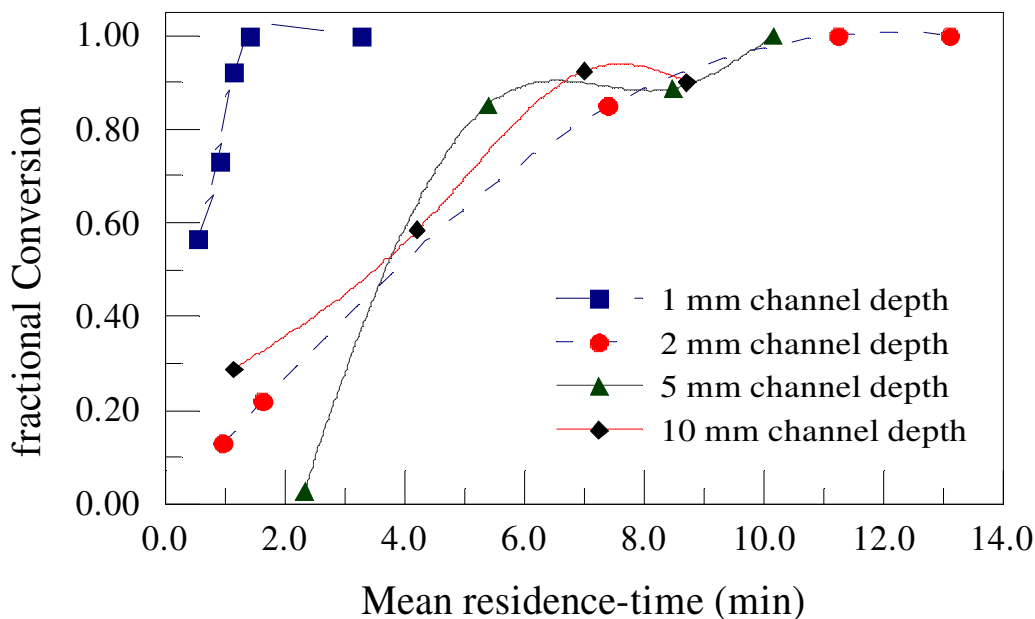
Figure 7. Effect of slit-channel depth on fractional conversion

3.4 Effect of Solid Catalyst

3.4.1 Qualitative results

In reporting our work under the solid catalyst, both qualitative and quantitative aspects of data collected will be referenced. Initially, we used and evaluated the solid oxides of zinc (ZnO), zirconium (ZrO_2), magnesium (MgO) and calcium (CaO) as supplied. After more than 3.5 hours at $65^{o}C$, the CaO showed best evidence of activity followed by ZnO. Based on this result, it was concluded that as the supplied oxides need some form of activation (thermal or otherwise) to stimulate them into activity. Further, the order of activity of the oxides (as supplied) was classified as follows:

$$ZrO_2 < MgO < ZnO < CaO$$
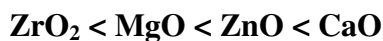
Since ZnO and CaO showed some activity towards biodiesel production, we considered the combination of the two for synergistic activities. Three methods of combination were examined as follows:

      (a) A mixture of CaO and ZnO in the ratio 1:2 by weight and used as prepared.

      (b) A mixture as in (a) but heated up to or greater than $600^{o}C$.

      (c) Mix $Zn(OH)_2$ with CaO and heat mixture together at more than $900^{o}C$ for
           between 8 - 24 hours.

The $Zn(OH)_2$ was prepared as follows: 0.69 g $ZnCl_2$ was dissolved in 28 ml water. Ammonia was added in the solution to precipitate $Zn(OH)_2$. The excess water was decanted and precipitate washed several times before mixing the precipitate with 1 gm CaO. The mixture was then heated to the required temperature and time.

Table 2: Identity of Calcium-Zinc Based Catalysts

Sample Identity	Active Components	Thermal Activation Method
A	33.3 wt % CaO + 66.7 wt % ZnO	No thermal treatment
B	33.3 wt % CaO + 66.7 wt % ZnO	Heated to $600^{o}C$ for 8 hr
C	$Zn(OH)_2$ mixed with CaO	Heated at at $900^{o}C$ for 24 hr

Following the activities described above, qualitative observation shows that the activity of catalyst A was not better than that of CaO alone. Catalyst B showed results better than those of catalyst A. The best result was obtained from catalyst C. Unfortunately, the Sandia analytical services could not analyze the samples for us for quantitative comparison of the conversion values achieved by these catalysts.

Significance of the Qualitative Studies

The significant milestone of the qualitative studies above is the development of a systematic method of using CaO as a catalyst for biodiesel production. We learned that the catalytic activity of as supplied CaO can be improved by annealing at $300^{o}C$ or higher (the higher the temperature the better the catalyst performance) for some hours. It was also demonstrated that the synergy between the combination of $Zn(OH)_2$ with CaO can yield a better performing solid catalyst.
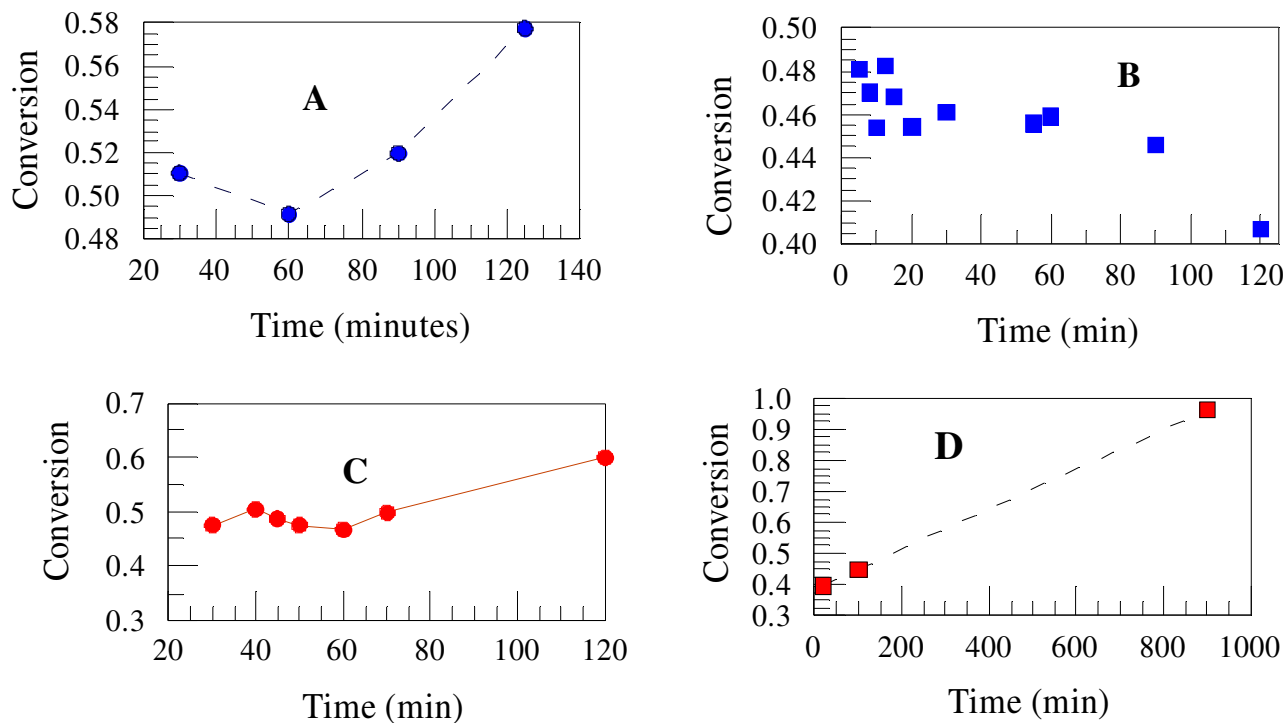
Figure 8. Conversion vs. time for solid catalysts:
A: CaO (300 C, 5 hours, 0.15 g);
B: HPA (600 C, 5 hours, 0.15 g);
C: HPA (560 C, 5 hours, 0.14 g);
D: Calcium gluconate (275 C, 3 hours, 0.15 g);

3.4.2 Quantitative results

Having determined that CaO is a promising solid catalyst, we evaluated other promising catalysts and combinations thereof. Based on the recent report of Chai et al.[6] , we evaluated heteropolyacid (HPA) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as a catalyst. In addition to these two, we also evaluated Calcium gluconate (unlike other catalysts, this is an environmentally friendly catalyst). For the preparation of HPA, the method described in the literature was followed (see Ref. 6). On annealing, however, we observed that the color of the crystals tended to depend on the annealing temperature. For instance at $560^{o}C$, white crystalline salt was obtained while greenish salt resulted at $600^{o}C$. The salt that resulted at $300^{o}C$ annealing was darkish blue. In all cases, the transesterification process produced whitish/milky color when the salt came into contact with methanol. Figure 8 shows conversion time curves for the solid catalysts.

3.4.3 Comparison of solid catalysts with NaOH liquid catalyst

The ultimate objective of our research effort is investigating the feasibility of a solid catalyst soybean oil transesterification in a biodiesel slit-channel reactor and the best method of coating the channel with the solid catalyst. We compared the performance of the solid catalysts to the homogeneous NaOH liquid catalyst by following the fractional conversion of triglycerides as a function of time in the presence of the different catalysts. The results obtained are shown in Figure 9.

All the solid catalysts used in Fig. 9 were annealed at 300 ^{o}C for 3 hours. The important deduction to make from the figure is that none of the solid catalysts showed catalytic activity comparable to that of homogeneous NaOH catalyst. Also, we observe that both the HPA and gluconate have high catalytic activity especially at the early stage of the transesterification process. Whereas the calcium gluconate tended to sustain its high activity, the HPA activity was not sustained for the duration of the time reported.
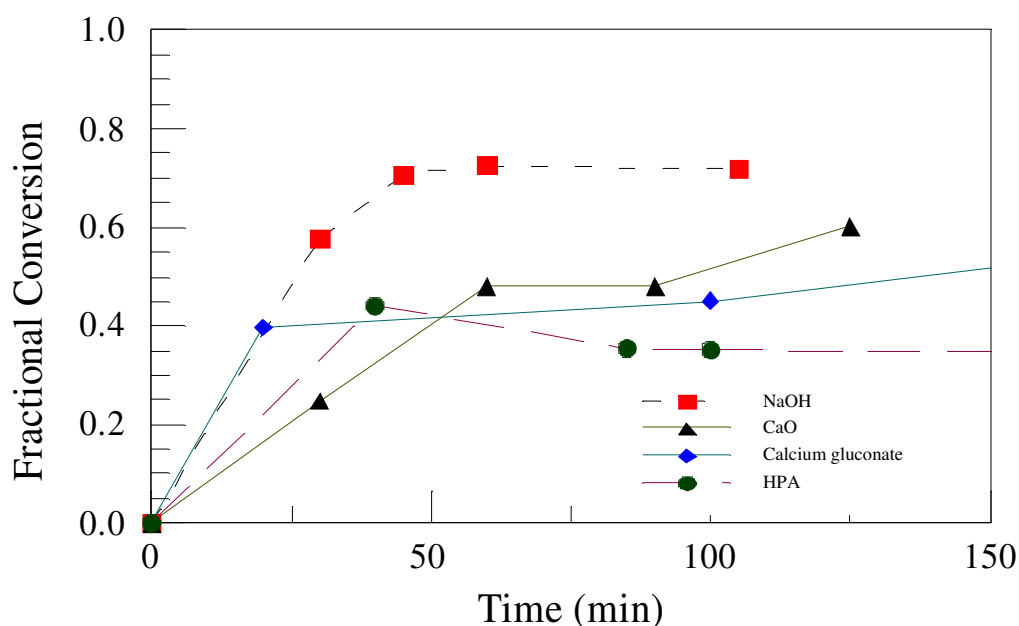
Figure 9. Batchwise conversion of soybean oil to biodiesel with different catalysts

For the soybean-oil-to-biodiesel experiments to be carried out in slit-channel reactors, we need a method to coat a selected solid catalyst (e.g., Calcium gluconate, CaO or HPA) on the channel surfaces. For the present work, we assessed the HPA mixed with cellulose. After undergoing thermal annealing, the cellulose-HPA mixture was weighed and added in a batch oil/methanol mixture. The results obtained were similar to those obtained in the absence of cellulose. However, more detailed experiments are required before a firm conclusion can be reached.

In addition to supporting the qualitative results, the quantitative data show that calcium gluconate is a very promising heterogeneous catalyst. Although limited in scope, preliminary data of solid catalyst mixed with polymer show promise of an approach for coating of the surface of the slit-channel reactors.

4. SUMMARY AND CONCLUDING REMARKS

Four slit-channel reactors with varying channel depth were fabricated and used to conduct exploratory experiments on converting soybean oil to biodiesel. We successfully produced biodiesel with different degree of conversion using the four slit-channel reactors fabricated. Results obtained from our exploratory experiments show that the slit-channel reactor performance (in terms of percent conversion) depends on the channel depth – lower channel depths perform better than channels that are deeper; that is, percent conversion of soybean oil to biodiesel increases with decreasing channel depth, as expected, due to more efficient mixing and and thus faster reaction as the channel becomes more shallow.

Six solid catalysts (CaO, MgO, ZnO, ZrO_2, calcium gluconate, and heteropolyacid or HPA) were evaluated for their effectiveness in soybean oil transesterification using batch reactors. Amongst these, CaO was confirmed as having the highest activity in catalyzing the transesterification reaction whereas calcium gluconate was demonstrated for the first time as a promising solid catalyst in our exploratory experiments using batch reactors.

In the present work, due to time and resource constraints, we didn't attempt to couple slit-channel reactors with solid catalysts in converting soybean oil to biodiesel. To realize the great potential of slit-channel reactors, however, the coating of the surfaces of the slit-channel reactor with a solid catalyst (or catalysts) needs to be investigated. Such a study will reveal any short-comings of coated solid catalyst over its performance in batch mode uncoated. A critical aspect of further research is the solid-catalyst deposition on the channel surfaces of a slit-channel reactor. Optimization of thermal treatment temperature for the solid catalysts also need to be investigated. Lastly, a predictive mathematical model of the slit-channel reactor needs to be developed; such a model, after being validated, can be exercised to reduce the number of experiments needed to study and understand the non-batch mode transesterification process.

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