Parametric Study on the Reactive Extraction of Rapeseed Oil for Biodiesel Production in a Batch Reactor.

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1. Introduction

In the conventional process to make biodiesel, the raw material is oil that has been pre-extracted from the seeds, and usually degummed and refined. However, it has been shown that transesterification of the oil can actually be carried out directly from the plant seeds without prior extraction [1]. In this scheme, macerated seeds are contacted directly with methanol and catalyst to produce biodiesel without the need of other solvents. This route will simplify the overall biodiesel process scheme and has the potential to improve the efficiency of the process as well as to reduce the production cost. Using this technique, the use of hexane to extract the oil can be eliminated as the extraction is being carried out by the reactant it self. This provides an added environmental benefit as hexane is classified as a hazardous air pollutant and contributes to the production of smog and global warming.

The overall objective of this research is to develop an integrated technology combining the extraction of vegetable oil from oilseeds with reaction of that oil to biodiesel in a one-step extraction/reaction process. The steps and parameters involved in the integrated extraction/reaction scheme differ from that of the conventional process in many ways. The fact that the reaction system is heterogeneous could alter the kinetics of the transesterification reaction. The mechanism on how the reaction and extraction occurs in the seeds is also not well understood. The parameters that affect extraction such as seeds pretreatment, particle size, moisture level, and solvent amount will also affect the yield of ester. The presence of other compounds in the seeds might also interfere with the transesterification reaction and the final ester and glycerol product might contain compound from the seeds that is soluble in methanol. Hence, the optimum values for methanol/oil molar ratio, catalyst concentration and temperature may differ between conventional transesterification and the combined reaction/extraction scheme.

In this study, investigations were carried out to understand the process parameters that affect the efficiency of the *in situ* process. Specifically, the effect of operating parameters such as molar ratio of alcohol to oil, particulate size, catalyst concentration, and moisture content were investigated.

2. Methods and Analysis

Materials

The rapeseeds were cultivated in the university farmland for the Newcastle University Agricultural Department. The seeds contain 45.9 wt% oil. The free fatty acid of the oil, was 3.35 wt % and the moisture content of the seeds was 6.7 wt %. Methanol used was of analytical grade with an assays of 99.95%.

Experimental Setup and Procedures

The experimental apparatus consisted of a two-neck round bottom flask containing the seed and the solvent, which was immersed in a temperature controlled water bath. An overhead stirrer with variable speed provided stirring for the system. An overhead condenser was placed in one of the flask neck to condense the evaporated solvent back into the system.

50 grams of rapeseed was grounded and sieved to a specific particle size. The seeds were then placed in the round bottom flask with a specific amount of methanol in which NaOH has been dissolved. The temperature used for the reaction is 60^{o}C and the methanol has been previously heated to this temperature before the start of the reaction. The stirring rate was kept at 150 rpm through out all the studies. After the reaction time was reached, glacial acetic acid was added to the reaction mixture to stop the reaction. The liquid was separated from the seeds using vacuum filtration. The seeds were washed with an additional 60 ml of alcohol to recover any products that stick to the seeds during the filtration step. The extract was then transferred to a rotary evaporator where the solvent was removed under vacuum at a temperature ranging from 60 – 90 ^{o}C . After the entire methanol was evaporated, the product consists of an upper layer of ester phase and a lower layer of glycerol phase. In order to separate between the two layers, the products were transferred to a separatory funnel where the lower layer was withdrawn from the bottom of the funnel. The mass of the total extract and the ester phase was recorded
The composition of the ester phase for each reaction time was analyzed using a gas chromatograph according to BS EN 14105:2003.

3. Results and Discussion

3.1 Progress of Reactive Extraction

Figure 1 shows the progress of the reactive extraction process. The extraction was very fast in the first 5 minutes whereby 50% of the oil is extracted out during this period. This could be due to very fast reaction of the oil at the particle surface with the excessive amount of methanol and the washing of the ester to the bulk phase. Analysis of the ester phase during the first 5 minutes shows that it contains some amount of mono and diglycerides but very little triglycerides. The

absence of significant amount of triglycerides at the early reaction times suggests that the reaction of oil to ester occurs either in the seeds particles or at the seeds surface which is then followed by the extraction of that ester or mono and diglycerides into the bulk methanol phase. After the first 5 minutes the extraction rate slows down. This could correspond to diffusional leaching of the ester from inside the solids particles which is a slower mass transfer step. The ester yield become almost constant after about 1 hour indicating that the equilibrium is reached between the concentration of ester in the particles and in the bulk methanol. The composition of the ester shows that it contains less than 2% mono and diglycerides which indicates that the conversion of oil to ester is very high in the reactive extraction process.

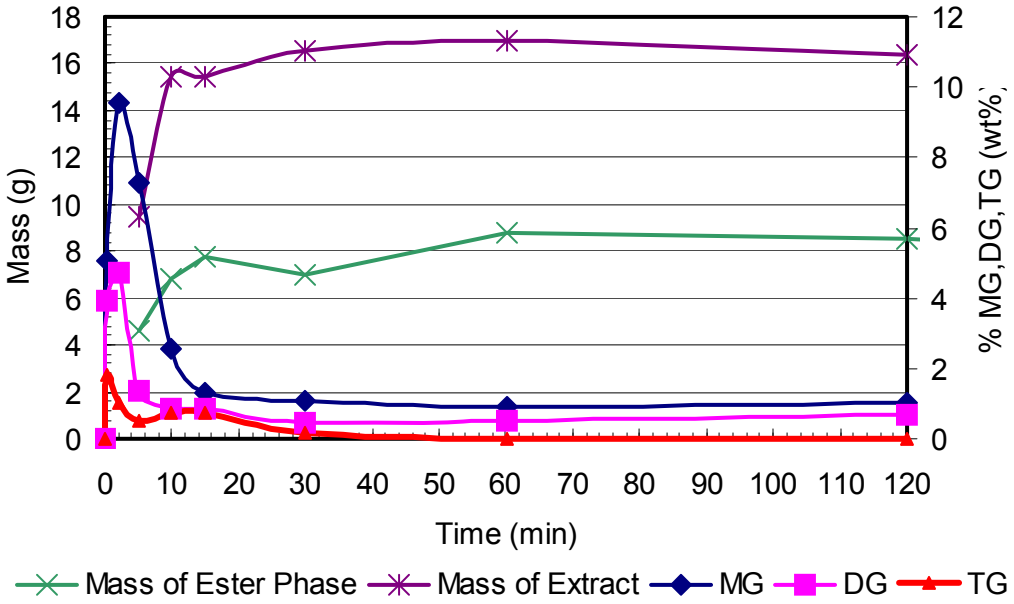

Figure 1- Progress of Reactive Extraction

3.2 Effect of Solvent to Oil Ratio

From the time study above it can be seen that under the particular process conditions, the equilibrium concentration of ester in the methanol phase should be reached by 1 hour. The effect of solvent to oil ratio is therefore studied after 1 hour reaction as shown in Figure 2. It can be seen that the amount of ester extracted increases with the amount of methanol used. As the diffusion process depends on the concentration gradient between the bulk phase and inside the particles, the more solvents that are used, the higher the concentration gradient and the more ester is extracted out. Using a lower ratio than 95 does not result in any significant biodiesel being produced. The ester yield reaches a maximum at 650:1 molar ratio. Further than this, emulsion exists between the ester and the glycerol phase and the amount of ester phase that can be physically separated

from the glycerol phase reduces. This could be due to the high amount of catalyst when high amount of solvent is used. However, if the emulsion is extracted using hexane, the yield of ester from the higher solvent to oil molar ratio is similar to the maximum achievable yield.

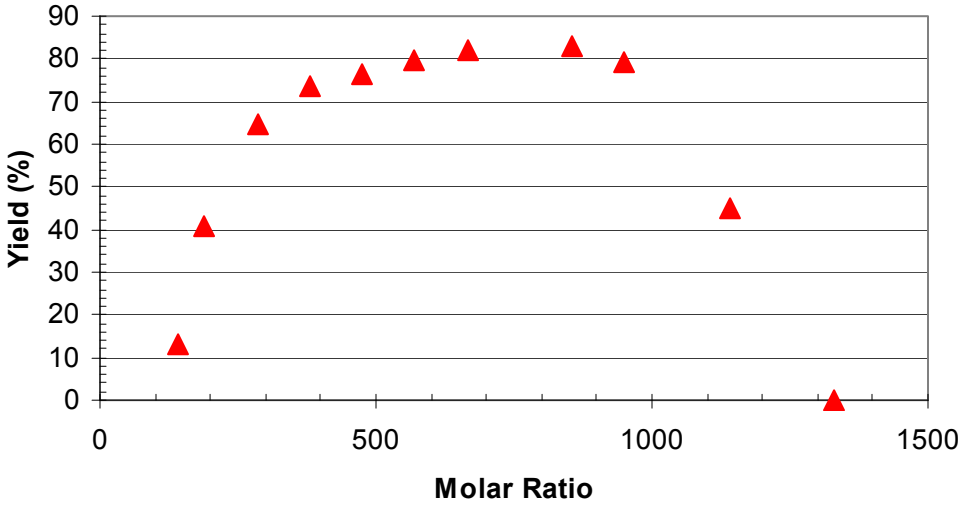

Figure 2 - Effect of Methanol to Oil Molar Ratio

3.3 Effect of Catalyst Concentration

The effect of catalyst concentration after a 1 hour reaction is shown in Figure 3. Using 0.05 m NaOH concentration, the maximum ester yield is achieved at about 1250 molar ratio whereas the maximum yield can be achieved at 650 molar ratio using 0.1 m NaOH. Therefore less solvent is required to achieve similar yield within the one hour reaction time for 0.1 m compared to 0.05 m NaOH concentration. Increasing the catalyst concentration to 0.15 m however causes a reduction in the yield. As shown in Figure 3, the amount of total extract for 0.1 and 0.15 m is similar but the ester yield is lower for 0.15 m. This could be caused by either the saponification reaction associated with high NaOH concentration or partial emulsification of the ester with the glycerol phase. Also it can be seen that at 0.15 m, the extract is completely emulsified at a much lower solvent to oil ratio than at 0.1m. Using 0.05 catalyst concentration on the hand does not result in any emulsification in the range of solvent to oil ratio studied.

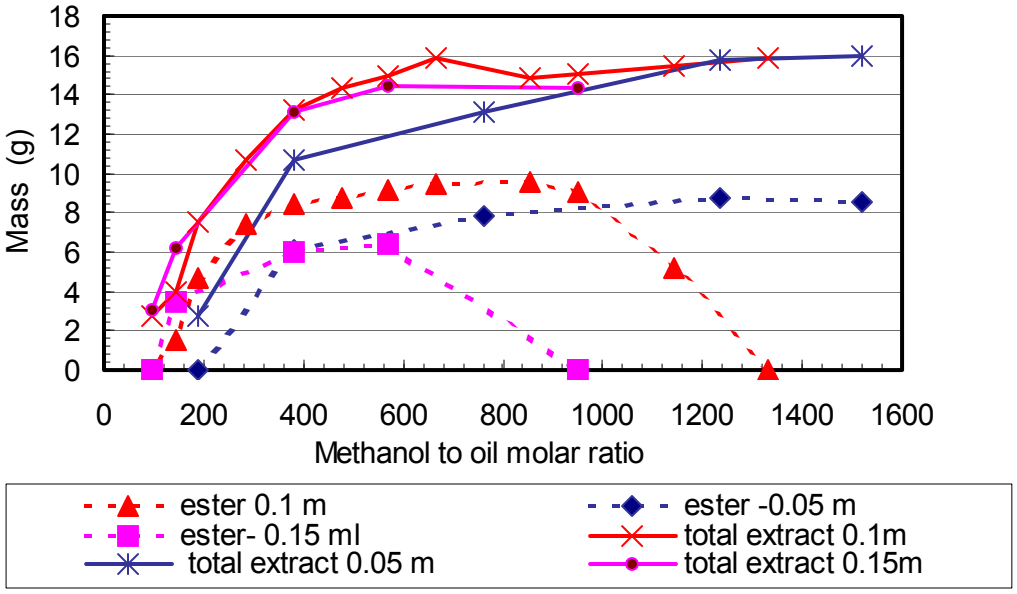

Figure 3- Effect of Catalyst Concentration

3.4 Effect of Particle size

The effect of particle size is seen in Figure 4 and 5. Reducing the particle size reduces the distance for the oil to diffuse out from the seeds particles and hence increases the rate of extraction. Therefore within the one-hour reaction, a lower particle size will give a higher yield as seen in Figure 4. However, at a longer time (5 hour), the yield for the larger particle size is similar to that of the smaller particles size as seen in Figure 5. This shows that particle size is important in determining the rate of diffusion but does not affect the final equilibrium yield for the rapeseeds particles

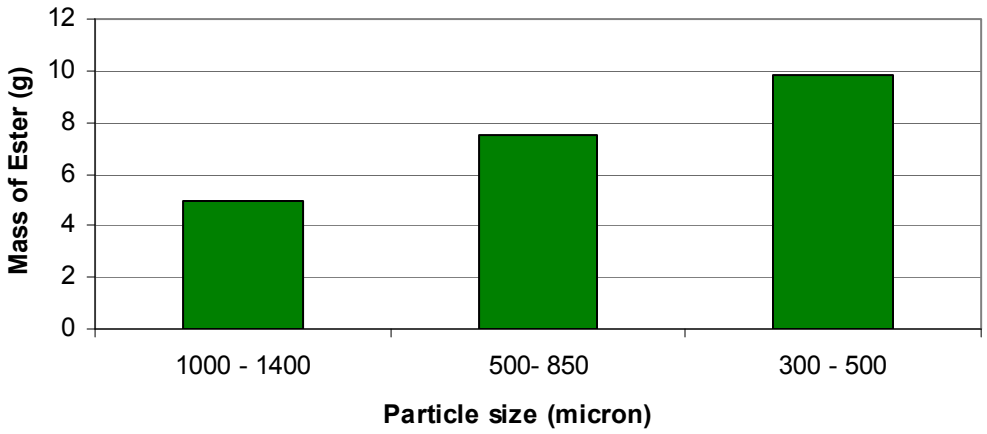

Figure 4- Effect of Particle Size

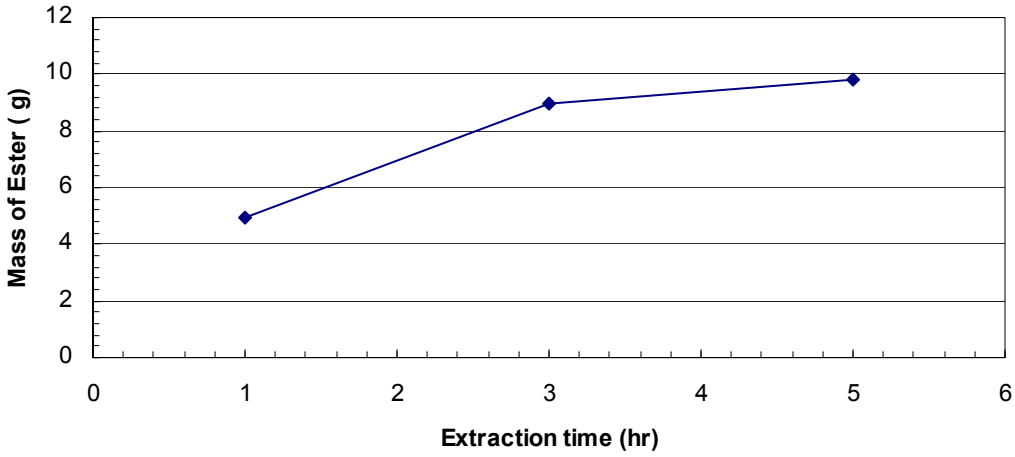

Figure 5- Yield of Ester versus Time for particle size 1000-1400 micron.

3.5 Effect of Moisture Content in Seeds

Previous literatures have shown that water adversely affect the transesterification reaction when NaOH is used [2]. The presence of water causes the saponification of both ester and triglycerides to soap and therefore reduces the yield of the reaction. Water was also reported to reduce the solvent capacity of some solvent such as ethanol [3]. It is therefore speculated that by drying the seeds to 0% moisture, the ester yield could be increased. The seeds initially have 6.7% moisture and were dried to 0% moisture in an oven at 104^{o}C until constant weight. The result of drying is shown in Figure 6. Contrary to the prediction, drying the seeds to 0% moisture does not result in an increase in

ester yield. The amount of solvent needed to achieve maximum yield also does not reduce when using dry seeds. This indicates that the amount of water in the seeds (6.7%) does not affect the transesterification and extraction process to any significant extent.

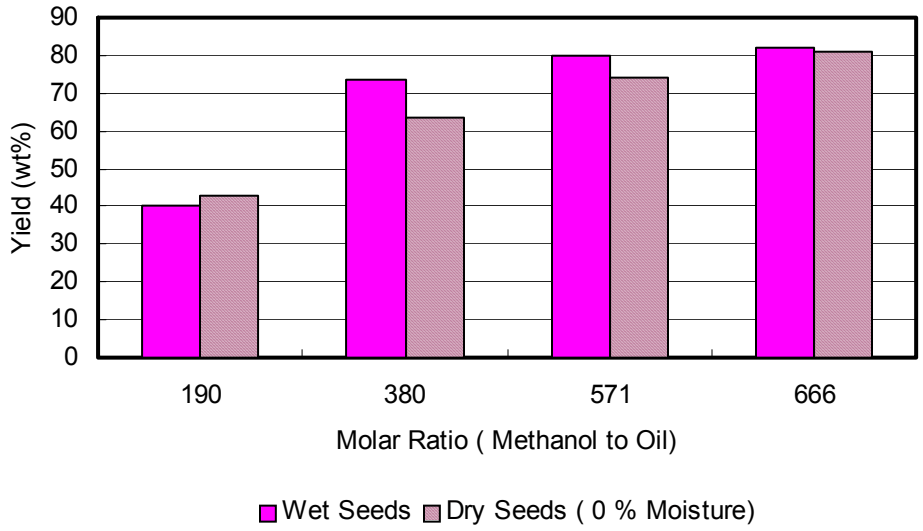

Figure 6 – Effect of Drying

4.0 Conclusions

The studies show that methanol to oil molar ratio and catalyst concentration affects the ester yield significantly. The equilibrium yield of ester is mainly determined by the methanol to oil molar ratio. The maximum ester yield is achieved at 650:1 molar ration and 0.1 m NaOH concentration. Smaller particle size affect the kinetics of the extraction but does not seems to alter the final equilibrium yield of ester. Reducing the water content of the seeds from 6.7% to 0% does not seem to present any significant effect to the ester yield.

References

[1] Harrington, K.J and D'Arcy-Evans, C., A comparison of Conventional and In Situ Methods of Transesterification of Seed Oil from a Series of Sunflower Cultivars, Journal of American Oil Chemist Society , v 81, n 2, p 83-89

[2] Haas, M.J., Scott, K., Moisture removal substantially improves the efficiency of in situ biodiesel production from soybeans, Journal of American Oil Chemist Society , v 84, 2007, p 197b-204

[3] Hron, R.J., M.S. Kuk, G.Abraham, and P.J.Wan, Ethanol extraction of oil, gossypol and aflatoxin from cottonseed, Journal of the American Oil Chemists' Society, v 71, n 4, 1994, p 417-421