

Preliminary Study on Extraction and Synthesis of Biodiesel from Jatropha Curcas Seeds and Soybean

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Abstract

Solvent extraction with hexane has been evaluated for extraction of oil from *Jatropha curcas* L. seeds and soybean. Experimentally, the effects of time, temperature and size on the extraction yield were investigated. It was found that oil extraction with hexane has high efficiency, while the extraction yield was affected by extraction time, temperature and size. Reduction in particle size, coarse to powder grinded, had effectively increased the extraction yield by more than 6.4%, whereas an increase in temperature from room temperature to 70°C moderately accelerated the extraction process for both *jatropha* and soybean. Continuous heating of the oil above boiling point (68°C – 70°) of solvent should be avoided as evaporation and degradation of oils components reduced the extraction yield. The optimum extraction yields obtained for both *jatropha* and soybean were 43% and 23% at 135 and 75 minutes respectively.

Transesterification of *jatropha* and soybean oils to produce *jatropha* oil methyl ester (JOME) and soybean oil methyl esters (SOME) were carried out. The process was carried out at reaction conditions; temperature 60°C and 70°C and at methanol to oil molar ratio 6:1. Potassium hydroxide (KOH) was used as a catalyst and reaction time of 60 minutes. Increasing temperature from 60°C to 70°C resulted in lower conversion to both JOME and SOME. Soybean oil shows better conversion compared to conversion of *jatropha* oil to methyl ester with most of the triglycerides of soybean oil was converted to methyl ester.

1.0 Introduction

As the worldwide energy demand is increasing, biodiesel, which is derived from vegetable oil, has become a potential renewable source of fuel to overcome the problem of finite source. Biodiesel is comprised of mono-alkyl ester of long chain fatty acid produced from triglycerides. The development of biodiesel is increasingly important as it is characterized by excellent fuel properties and can be used by existing combustion engine with little or no modifications. It is also environmental friendly as it is biodegradable, non-toxic and has low emission profiles as compared to petroleum.

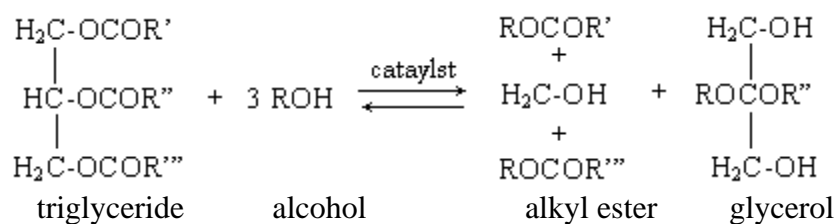
Jatropha curcas is today viewed as a challenge species as its seed has high oil content (30-60%) that can produce renewable biodiesel. In addition, *Jatropha curcas* is a drought resistant tropical tree that can live up to 50 years and growing on marginal soils. However, research on *Jatropha curcas* is relatively new compared to soybean. Soybean with around 20% oil content

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on dry basis has high protein content and is one of the world largest oilseed crops and it is commercially available.

Biodiesel (methyl ester) can be derived from *Jatropha curcas* seed oil and soybean oil. The production of *jatropha curcas* seed oil methyl ester (JOME) and soybean oil methyl ester (SOME) involves extraction process and transesterification reaction. Extraction of vegetable oil from the seed or bean is necessary before biodiesel can be produced. Various extraction processes such as pressing, aqueous extraction, supercritical fluid extraction and solvent extraction can be used for oil extraction. However, as the industry becomes competitive, the technology of oil extraction must advance in order to minimize production costs and, at the same time maintaining high efficiency in oil production. By considering the cost and efficiency, solvent extraction is the most common, most efficient and most suitable technique in producing oil for biodiesel production. Solvent extraction process is dependent on the nature of the solvent and oil, the temperature of extraction, contact time between solvent and particle size of the grinded meal, and pretreatment conditions of the seed or bean. Some of these factors will also affect the properties of the extracted oils.

Transesterification reaction describes the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety [1]. The overall process is reversible reaction and the reaction of the transesterification of the vegetable oil is shown in the Figure 1.0.



Where R = alkyl group of the alcohol and R', R'', R''' = carbon chain of the fatty acid

Figure 1.0 General equation for transesterification of vegetable oil

The presence of a strong catalyst (typically a strong base or acid) accelerates the adjustment of the equilibrium where a high yield is achieved under the condition of excess alcohol. In this research, a base catalyzed transesterification reaction is preferred since it can be carried out at low temperature and pressure to give a high conversion of methyl ester with minimal side reaction and shorter reaction time.

The objectives of this work are to study the extraction and synthesis of biodiesel from *jatropha curcas* seeds and soybean. Investigation on the effects of time, temperature and size in solvent (hexane) extraction on the level of oil yield obtainable were carried out. The effects of different temperatures in transesterification with potassium hydroxide (KOH) on the yield of methyl esters obtained from *jatropha* seed and soybean were also examined.

2.0 Materials & Method

2.1 Materials

The jatropha seeds were collected from Kelantan, Malaysia while soybeans were imported from China and were purchased from the market. Hexane, methanol and potassium hydroxide (KOH), ethyl acetate and N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) were obtained from environment lab of Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia.

2.2 Extraction

The seeds of soybean were dried in an oven at 50°C for around an hour and dehulled. Then the seeds of jatropha and soybean were grinded with a sieve plate and shaker using 0.5mm sieve plate. Soybean particle above the sieve was collected and was used as a coarse size sample. The extraction was performed in a modified Soxhlet extractor where a 250-ml-three-neck flask equipped with a thermometer, a sampling port and a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator and a vacuum trap. The reactor was immersed in a temperature-controlled oil bath and was under constant stirring provided by a magnetic stirrer. 20g of grinded meals were transferred into the extractor together with 140 ml of solvent (hexane). The extraction process was carried out with jatropha grinded meal at 70°C for extraction times of 2-4 h. Soybean grinded meal was extracted at the room temperature for extraction times of 1, 3 and 6 h and also at 70°C for extraction times of 1-4 h. The extraction of coarse size grinded soybean meal was also carried out for 1 h extraction time at room temperature. The residue was separated from the micelle by a vacuum filtration. Subsequently, the hexane was separated from the oil and recovered by using rotary vacuum evaporator (N-1N W) where the temperature of evaporation was set 70°C. The oil obtained was weighed and the oil yield was calculated.

2.3 Transesterification

A molar ratio of methanol to oil was set at 6:1 and the catalyst (KOH) amount was fixed at 1.5 wt% of seed oil for the transesterification process. The reaction was performed with a 250-ml-three-neck flask filled with 4.5 ml of methanol. Subsequently, 0.3g KOH pellets were added and the mixture was swirled for half an hour or until all pellets were dissolved. 20g of extracted grinded meal oil were then transferred into 250-ml-three-neck flask. The flask was equipped with a thermometer, a sampling port and a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator and a vacuum trap. The flask was immersed in a temperature-controlled oil bath and was under constant stirring provided by a magnetic stirrer. The reaction was carried out for jatropha oil and soybean oil at 60°C and 70°C with reaction times of 1 and 2 h. JOME and SOME were obtained after the phase separation of the reaction mixture in a separatory funnel. The glycerol layer was withdrawn from the bottom layer, leaving methyl ester for subsequent purification process.

2.3 GC-Analysis

Qualitative and quantitative analyses of the specimens of jatropha oil, soybean oil, JOME and SOME were carried out by the gas chromatography (GC) method. A drop of sample was kept in a small bottle prior to analysis. 1 ml of ethyl acetate was added and was shaken for 5 minutes. Then, 0.5 ml of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was added and the

bottle was immersed into a water bath of 40⁰C for at least 10 minutes. Then the sample was injected into the GC.

3.0 Results and Discussion

3.1 Effects of Extraction Parameters

Solvent extraction depends largely on the type of the solvent used, the ratio between the solvent and grinded meal, the temperature and pressure of extraction, extraction time, particle size and pretreatment conditions. However, the three most important parameters affecting the oil yield are the size of the grinded meal, the contact time and the temperature of the solvent. Other parameters are maintained constant.

Throughout the experiment, the ratio of solvent (ml) to grinded meal used (g) was set at 7:1. Earlier research by Akaranta[2] had found that the ratio did not influence the efficiency of oil extraction markedly. Therefore, the ratio of solvent to grinded meal was fixed at 7:1. Batch operation was used in the research, as it is suitable for small samples. The mixture was stirred continuously to increase the diffusion rate. The size of the grinded soybean and jatropha played an important role in oil extraction process. By reducing the size of the particles to the smallest size feasible, the intimate contact area is maximized. Figure 3.0 shows the effect of particle size on the oil yield level obtainable for soybean extraction at room temperature and 1 hour extracting time.

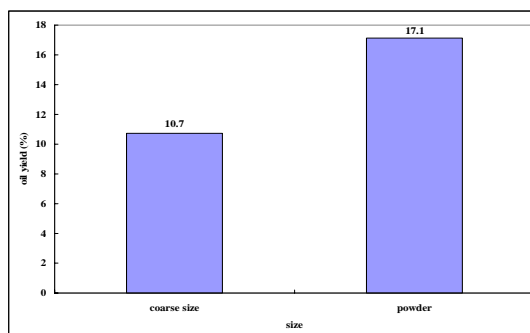


Figure 3.0 The effect of particle size on the oil yield level obtainable for soybean extraction at room temperature.

As shown in Figure 3.0, the oil yield obtained from extraction with coarse size grinded soybean is less than the oil yield obtainable from powder size grinded soybean. The percentages of oil yield obtainable are 10.7% and 17.1% respectively. The percentages of oil yield obtained are in agreement with the effect of particle size. As the size increases, the contact area decreases and resistance to the solvent to transport inside the particles increases. Hence the ability for diffusion of soybean oil from grinded soybean meal to the solvent becomes lower. The change in size contributes markedly to the oil yield obtainable. The oil yield from the extraction with powder size soybean is 6.4% more compared to the coarse size soybean.

Besides particle size, contact time and temperature are also an important factor that would affect the oil yield level. In Figure 3.1, the graph shows that the extraction at room temperature requires a longer time to achieve the maximum solubility. The graph also shows

that the extraction rate increased rapidly during the initial stage for both jatropha and soybean grinded meals.

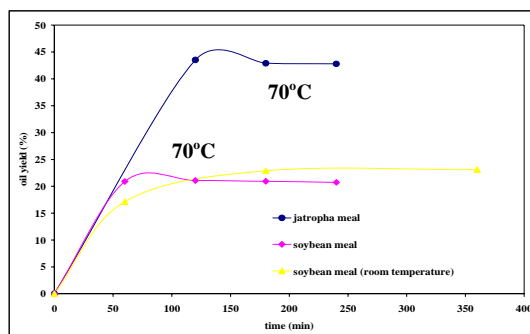


Figure 3.1 The effect of contact time and temperature for different powder size grinded meal on oil yield

As shown in the graph, the percent oil yield increases rapidly at the initial state as the extraction time increases. This is because the concentration of soybean oil in the solvent was low at the beginning of oil extraction process, thus the oil diffusion occurs rapidly from the meal to hexane phase. When time increases, the concentration of oil in solvent increased and caused the diffusion rate to decrease. As soon as the maximum solubility was reached or when the maximum amount of extractable oil was reached, the oil yield level remained the same even the extraction time was extended. The plotted graph for extraction of soybean at room temperature shows the maximum amount of oil extractable is reached at the contact time of 200 minutes. After 200 minutes, extraction is independent of time where the oil yield will remain the same.

Both plotted lines for extraction of soybean and jatropha oil illustrate that the oil yield decreases as time increases after the maximum value is reached. This happened because extraction was carried out at 70°C where continuous heating of the oil and solvent had caused evaporation of solvent and degradation of protein. Solvent (hexane) with a boiling range of 68-70°C may also behaved as a partial supercritical fluid as the boiling point was reached when extraction was being carried out at 70°C.

In extraction process, temperature is an important factor that had to be taken into consideration, as it will affect the efficiency of extraction. Generally, increasing in temperature enhance solubility of oils in solvents [2]. However, the statement is only true for extraction that being carried out below boiling point of solvent. The experiment also showed that after 1 hour of extraction, the oil yield at 70°C was higher then at room temperature. Hence shorter contact time is more efficiently carried out at high temperature. This is because at higher temperature, the solvent viscosity becomes lower and the rate of diffusion of oil in solvent is higher. As a result, the oil yield obtained at 70°C (20.9%) was higher than at room temperature (17.1%).

For a continuous extraction process, which was carried out at 70°C, the profile of oil yield obtainable is slightly different from the profile obtained from extraction at room temperature. At high extraction temperature, the maximum oil yield could be achieved in a shorter time. However, the maximum percent oil yield at 70°C was lower compared to the extraction at room temperature. At high temperature, less amount of solvent is available (in liquid phase) for the extraction since most of the solvent had vaporized. Besides that, solvent hexane with

a boiling range of 68-70^oC may also behave as a partial supercritical fluid as the boiling point was reached when extraction was being carried out at 70^oC. At the same time, the degradation of oil may occur as the oil was heated for a long time. Degradation of oil might form components, which could not be extracted. Consequently, the oil content was reduced and led to the decrement in weight of oil obtainable. Therefore, the percent oil yield decreased slightly as the oil was heated for a long time.

The graph also shows that grinded soybean took shorter time to reach a maximum value compared to the grinded jatropha meal. This is due to the lower oil content in soybean meal. Jatropha seed contains 30-60% of oil on weight basis while soybean only has 15-24% of oil on weight basis. Therefore, a longer extraction time is required in order to achieve the maximum oil yield obtainable. As time increases, the concentration of oil in the solvent also increases. Subsequently, the diffusion rate decreases, thus a longer time was needed for extracting oil from high oil content grinded meal. The soybean oil extraction at 70^oC has a maximum oil yield level of 22.3% at 75 minutes. Whereas jatropha oil extraction at 70^oC has a maximum oil yield level of 45.5% at 135 minutes.

3.2 *Effect of Temperature on Transesterification*

The transesterification reaction between oil and methanol is a reversible reaction as shown in Figure 1.0. The presence of a catalyst such as KOH is necessary to increase the concentration of alkoxide and protonated catalyst. The lack of nucleophilic to attack the alkoxide at carbonyl group of the triglyceride (oil) will cease the transesterification process. Thus, the triglycerides cannot be converted fully to methyl ester and glycerol.

Figure 3.2 shows the weight percentages of methyl ester (yield) from the transesterification of the oil at 60 and 70^oC. The graph shows that transesterification at 60^oC give higher yield of methyl ester for both Jatropha and soybean oil. The yields of JOME and SOME at 60^oC were 90.2 and 95.7% w/w respectively. While at 70^oC the yields of JOME and SOME are lower at 61.9 and 85.1% w/w respectively.

When the temperature of the reaction increases, molecules are moving at higher velocities. Thus, increases the number of collisions between molecules resulting in enough energy to break and reform the chemical bonds. Therefore, an increase in the temperature should increase the rate of transesterification reaction. However, when the operating temperature is near to the methanol boiling point (68^oC), the results obtained are opposite. The transesterification at 70^oC gave a lower yield of methyl ester. This is mainly due to the insufficient amount of methanol available for transesterification reaction, thus promotes the backward reaction and reduces the yield (Figure 3.2). In addition, lower volume of liquid phase methanol contributes to the decrement of alkoxide ions necessary to initiate the reaction.

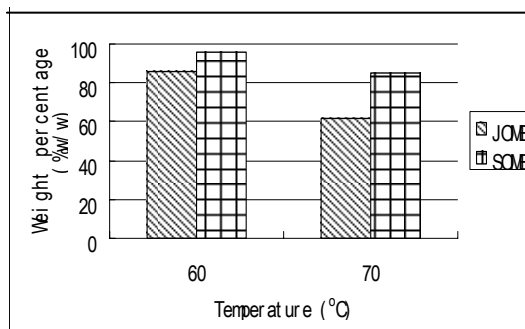


Figure 3.2 Weight percentage of methyl ester to Jatropha and soybean oil at 60 and 70°C. Condition: molar ratio of methanol to oil, 6:1; 1.5wt% KOH by weight of oil was used as base catalyst.

3.3 Conversion of JOME and SOME

The main purpose of transesterification process is to reduce the high viscosity of triglycerides to produce a lower viscosity biodiesel. The viscosity of JOME and SOME produced is related to the fatty acid compositions in the liquid. Table 1 shows the mean fatty acid component of JOME and SOME by chain length, which was obtained from GC-analysis method. The viscosity of JOME and SOME can be estimated by referring to the composition of fatty acid in the methyl ester.

Table 1 Mean fatty acid component of JOME and SOME by chain length

Fatty acids	Weight percentage of fatty acids (wt%)			
	JOME		SOME	
	60°C	70°C	60°C	70°C
Long chain, saturated (C16:00 and C18:00)	16.0	16.7	10.9	13.4
Long chain, unsaturated (C18:01 and C18:02)	84.0	83.3	89.1	86.6

Saturated fatty acids are solid whereas unsaturated fatty acids are liquid at room temperature. Therefore, methyl ester with higher saturated fatty acids has a higher viscosity. Table 1 shows that JOME has slightly higher percentage of saturated fatty acids compared to SOME. Thus, JOME has slightly higher viscosity than SOME. The percentages of saturated fatty acids in both JOME and SOME were high when the transesterification temperature was at 70°C. At high temperature, the double bonds in fatty acids may have been broken down to saturated fatty acids thus increases the saturated fractions.

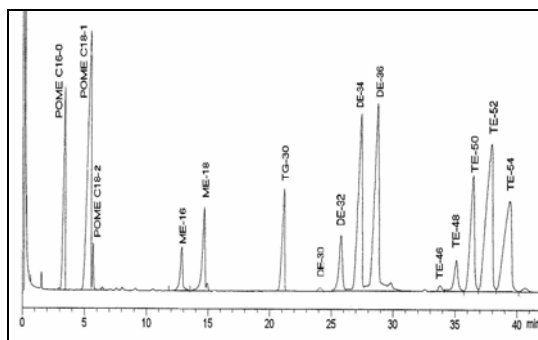


Figure 1 GC Chromatogram of reaction products: POME-palm oil methyl ester, ME-monomlycerides, DE-diglycerides, TE-triglycerides; TG 30 (trilaurin) is internal standard

4.0 Conclusion

In solvent extraction process using hexane, reducing the particle size to the smallest size feasible is found to be the most effective way to increase the extraction rate as it maximizes the intimate contact area. Experimentally, extraction yield was increased by more than 6.4%. Extraction rate was found to be dependent on the temperature. As the temperature increases from room temperature to 70°C, the extraction rate increased moderately. However, when continuous heating was carried out near to the boiling point of the solvent, the solvent evaporated and not enough solvent available for extraction. At 70°C, the optimum yield for low oil content grinded soybean was 23% at 75 minutes and for high oil content grinded jatropha seed was 43% at 135 minutes. The oil yield obtainable decreased after it attained the optimum extraction time. The oil yield obtained increased with time but as the extraction time increased beyond 2 hour, the extraction rate decreased appreciably.

Transesterification of Jatropha and soybean oil with methanol by using alkaline catalyst of 1.5 wt% KOH was reported to be more efficient at 60°C compared to 70°C. The methanol to oil molar ratio was in excess at 6:1 to promote the forward reaction to form fatty acid methyl ester. After transesterification, the viscosity of biodiesel can be reduced as close as the viscosity of diesel. Vegetable oil cannot be used directly in diesel engines at room temperature because their high viscosity could cause clogging of fuel lines, filters and injectors. Therefore, to hinder the problem vegetable oil must be converted into biodiesel through the process of transesterification of oil with alcohol in the presence of a catalyst. Various sources such as edible oils, jatropha oil, animal fats and waste vegetable oils can be used as a starting material of biodiesel.

Jatropha curcas has considerable high potential to be used in the production of renewable biofuel as quantitatively jatropha seed has a high content of oil and undoubtedly minimized the production costs. However, the research on the improvement of jatropha seed biodiesel quality is necessary before it can be widely used.

References

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