Green bio-oil extraction for oil crops

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Abstract. The move towards a green bio-oil extraction technique is highlighted in this paper. The commonly practised organic solvent oil extraction technique could be replaced with a modified microwave extraction. Jatropha seeds (Jatropha curcas) were used to extract bio-oil. Clean samples were heated in an oven at 110°C for 24 hours to remove moisture content and ground to obtain particle size smaller than 50µm. Extraction was carried out at different extraction times 15 min, 30 min, 45 min, 60 min and 120 min to determine oil yield. The bio-oil yield obtained from microwave assisted extraction system at 90 minutes was 36% while that from soxhlet extraction for 6 hours was 42%. Bio-oil extracted using the microwave assisted extraction (MAE) system could enhance yield of bio-oil compared to soxhlet extraction. The MAE extraction system is rapid using only water as solvent which is a non-hazardous, environment-friendly technique compared to soxhlet extraction (SE) method using hexane as solvent. Thus, this is a green technique of bio-oil extraction using only water as extractant. Bio-oil extraction from the pyrolysis of empty fruit bunch (EFB), a biomass waste from oil palm crop, was enhanced using a biocatalyst derived from seashell waste. Oil yield for non-catalytic extraction was 43.8% while addition of seashell-based biocatalyst was 44.6%. The pH of bio-oil increased from 3.5 to 4.3. The viscosity of bio-oil obtained by catalytic means increased from 20.5 to 37.8 cP. A rapid and environment friendly extraction technique is preferable to enhance bio-oil yield. The microwave assisted approach is a green, rapid and environmental friendly extraction technique for the production of bio-oil bearing crops.

1. Introduction
Research towards a green, efficient and sustainable oil extraction technique and the conventional soxhlet extraction using hazardous chemicals was compared. Conventional extraction techniques are laborious, time consuming, involving large amounts of solvent, and ultimately, may cause some target molecule degradation and partial loss of volatiles. The use of a non-conventional technique such as microwave assisted extraction (MAE) using water as extractant and a green technique using seashell waste as biocatalyst was studied. The main advantages of green technology such as higher yield of bio-oil, reduction in extraction time and quality improvement of bio-oil are evident in this study. However each technique requires an optimised operating condition in order to obtain high yield and good quality of bio-oil. Efficient cost effective extraction is often not only a matter of technique and
extraction conditions, in fact the type of equipment such as microwave and reactor can strongly affect oil yield [1].

MAE was used to obtain bio-oil from *Jatropha* crop and MAE is more favourable compared to Soxhlet extraction (SE). MAE does not consume organic solvent, low cost and has extremely shorter extraction time compared to SE. MAE showed shorter reaction time compared to SE with similar yield of 40 % and 48 % [2]. Also, the catalytic application for extraction using pyrolysis technique enhanced yield and quality of bio-oil. Rohim *et al.* [3] pyrolyzed empty fruit bunch (EFB) of oil palm in a fixed bed reactor with waste eggshell to determine the effect of amount of catalyst loading and pyrolysis conditions on the oil yield. The maximum bio-oil yield was 37 % at 500 °C of pyrolysis temperature and 10 % of catalyst loading.

Extraction of bio-oil from non-edible oil crop should be efficient and sustainable. Therefore, to maximize the desired product quality and quantity it is important to minimize costs and environmental concerns. This study is aimed to evaluate bio-oil extraction from *Jatropha curcas* and empty fruit bunch (EFB) using microwave assisted extraction and fixed bed reactor to obtain high yield and quality of bio-oil and to investigate the effect of the seashell waste biocatalyst on the bio-oil production.

### 2. Materials and Methods

#### 2.1 Microwave assisted extraction (MAE)

**2.1.1. Sample preparation.** *Jatropha curcas* seeds were supplied by Agrotechnology Centre at University Malaysia Perlis situated north of Malaysia. Only fully ripened *Jatropha curcas* seeds were collected, cracked and the shells were removed. White and ripe seeds were selected while damaged seeds were discarded. The seeds were cleaned and dried at 105 °C for 30 minutes. Ground seeds were sieved through 500 µm sieves to obtain a uniform powder for the extraction process.

**2.1.2. Experimental.** 10 g *Jatropha* seed powder was placed in 500 mL round bottom flask and placed inside microwave cavity space. A condenser was attached to the round bottom flask. An open vessel microwave system operating at 700 watt maximum power with frequency 2450 MHz was used. The parameters studied were extraction time (60, 80, 100, 120, and 140 minutes), microwave power (200, 300, 400, 500, 600 and 700 watts) and amount of water (70, 100, 130, 160, 190, 210 mL). The extracted oil from MAE was separated from solid residue by vacuum filtration using Buchner filtration assembly using Whatman filter paper No. 1. The complete separation of oil from water was done in Rotavapor (BUCHI R-205) fitted with a controlled temperature oil bath (BUCHI B-490). Oil yield was calculated as follows:

\[
\text{Oil yield (\%) = } \frac{m_o}{m_s} \times 100
\]

\( m_{o(g)} \) - The mass of ground *Jatropha* seeds

\( m_{o(g)} \) - The mass of oil yield
2.1.3. Physico-chemical analysis

2.1.3.1 Acid value. 2 g of oil was weighed into 250 mL conical flask. 20 mL of neutralize alcohol was mixed with the oil. The mixture was heated for 3 minutes using a water bath. The mixture was allowed to cool down and titrated with 0.1N alcoholic potassium hydroxide solution. Few drops of phenolphthalein were added as an indicator. A blank sample was titrated simultaneously.

2.1.3.2. Free fatty acid (FFA). FFA is the amount of sodium hydroxide or potassium hydroxide (in milligrams) needed to neutralize the free acids in one gram of sample. Usually free fatty acid (FFA) is expressed as oleic acid percentage according to equation below:

\[
\% \text{ FFA as oleic acid (C18:1)} = \frac{28.2 \times N \times V}{W}
\]

Where
- \(N\) = Normality of NaOH solution;
- \(V\) = Volume of NaOH solution used in mL;
- \(W\) = Weight of sample;

5 g of Jatropha oil sample was placed into 250 mL conical flask. 50 mL of neutralised solvent was mixed with the oil. The mixture of Jatropha oil sample and neutralised solvent was heated at 40 °C on the hot plate. The sample was titrated with 0.1 N standard NaOH solutions while continuously shaking the flask gently until the first permanent pink colour was observed and persisted for 30 seconds.

2.1.3.3. Iodine value. 0.2 g Jatropha oil was weighed into a glass vial. The vial was then transferred into 500 mL flask. 20 mL of cyclohexane was added into the glass vial. 25 mL of Wijs solution was added followed by insertion of stopper. The mixtures were gently shaken and kept in the dark for 1 hour. 100 mL of water and 20 mL of the potassium iodide solution was added into the mixture. It was titrated with the standard sodium thiosulphate solution (Na\(_2\)S\(_2\)O\(_3\)). Titration was considered completed when the yellow colour of the mixture disappeared. Subsequently, 2 mL of the starch indicator was added and the titration was prolonged while shaking the vial vigorously until the blue colour disappeared. The blank sample was also carried out simultaneously with the test samples.

2.1.3.4. Peroxide value. 2 g Jatropha oil was weighed and mixed with 30 mL acetic acid-chloroform (3:2 v/v) in conical flask. 0.5 mL of saturated potassium iodide was pipetted into flask. The flask was
kept swirling for about 1 minute before addition of distilled water. The starch solution which was prepared was added to the solution drop wise. Titration of the solution was done by adding 0.01 N sodium thiosulphate solutions (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}) slowly with continual and mild shaking. Vigorous shaking of the solution during titration when approaching the end-point to unfetter the remaining iodine from the chloroform layers. Carefully, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution was added drop wise until the blue color vanished. Simultaneously, titration of the blank sample was similarly determined.

2.1.3.5. Saponification value. 2 g of Jatropha oil was weighed precisely into 250 mL round bottom flask. 25 mL of 0.5 N alcoholic potassium hydroxide solutions were added into the oil. The mixture was refluxed gently using water bath with condenser attachment for 1 hour. The mixture was allowed to cool for 30 minutes. The mixture was titrated with 0.5 N hydrochloric acid solution using phenolphthalein as indicator. Titration of blank sample was similarly determined.

2.1.3.6. Fatty acid composition. The determination of fatty acid composition was analyzed by conversion of oil to fatty acid methyl esters prepared by adding 950: 1 of n-hexane 50 mg of oil followed by 50: 1 of sodium methoxide. The mixtures were vortex for 5 s and allowed to settle for 5 min. The top layer (1: 1) was injected into a gas chromatograph (Model GC-14A, Shimadzu Corporation, Kyoto, Japan) equipped with a flame-ionisation detector and a polar capillary column (BPX70 0.25), 0.32 mm internal diameter, 60 m length and 0.25: m film thickness (SGE Incorporated, USA) to obtain individual peaks of fatty acid methyl esters. The detector temperature was maintained at 240 °C and column temperature at 110 °C held for one minute and increased at the rate of 8 °C /min to 220 °C and held for one minute. The run time was 32 minutes. The fatty acid methyl ester peaks were identified by comparing their retention time with the standards. Relative content of fatty acid was calculated based on the peak area of a fatty acid species to the total peak area of all the fatty acids in the oil sample.

2.2 Fixed bed reactor
2.2.1. Sample preparation. The empty fruit bunch (EFB) was obtained from a palm oil mill located in Kedah, North Malaysia. The sample was cleaned and chopped into smaller sizes and dried at 105 °C for 24 hours in an oven. The sample was ground using a crusher and then sieved to obtain desired particle size.

Calcium oxide (CaO) used as catalyst in this study was collected from nearby seaside and washed with distilled water and dried in oven for 24 hours at 110 °C. The seashells were finely ground. The powdered sample was sieved using stainless steel test sieve. The calcium oxide was prepared by calcinations of the sea shells at a temperature of 800 °C in the furnace for 2 hours. The calcined sample was cooled in a desiccator, the CaO was again ground in grinder. The biocatalyst was stored in desiccators before analysis.

2.2.2. Experimental. Extraction of sample was carried out using a fixed bed reactor system. The components of the system were a bucket, furnace, nitrogen cylinder, condenser and thermocouple, to monitor reaction temperature and attached with the chiller/refrigerator bath for cooling. The sample was placed in the reactor bucket and the weight of the reactor tube with sample was recorded. The chiller/refrigerator bath temperature was set up at 0 °C to make sure the condenser was cooled. The reactions such as pyrolysis temperature and nitrogen flow rate were set up prior to the experiment. Nitrogen was allowed to purge for 30 minutes.

The yield obtained from the experiment was weighed. The mass of the reactor tube with biochar and glass wool were also weighed. After production of oil, the products obtained were weighed according to equations (3)-(5).
Biochar yield (%) = (char product (g)) / (EFB sample (g)) \times 100\% \quad (3)

Bio-oil yield (%) = (liquid product (g)) / (EFB sample (g)) \times 100\% \quad (4)

Gas yield (%) = 100\% - (Biochar yield (%) + Bio oil yield (%)) \quad (5)

2.2.3. Catalytic pyrolysis. The experiment to study the effect of addition of catalyst on pyrolysis yields was conducted by mixing the EFB with different weight of the catalyst at 5, 10, 15, 20 wt. % maintained at optimum pyrolysis condition. The liquid product was collected and weighed. The bio-oil was obtained using rotary evaporator at a temperature of 58 °C in which the solvent was evaporated and removed. The solid biochar was collected and weighed. The syngas yield was calculated from the balance of overall material.

2.2.4. Characterization of bio-oil
2.2.4.1. pH. In order to evaluate the corrosive property of the bio-oil products, the pH of the bio-oil was measured using a pH meter. The electrode was directly dipped into bio-oil sample. The recorded value was expressed as a pH of bio-oil.

2.2.4.2. Viscosity. The viscosity of the pyrolytic oil was determined at 25°C using rheometer (HAAKE Rheostress 1). Cone and plate type (Measuring Cup Z 43 (Series 1) and plate PP 35 Ti, D=35mm geometry was used to determine the viscosity where temperature was controlled accurately within 0.05°C by HAAKE DC-50 temperature controller. A series of rheological data were collected and the average was recorded as viscosity of the oil.

3. Results and Discussion
3.1. Effect of extraction time on Jatropha oil yield
All the results obtained were presented in tables 1, 2 and 3 for extraction time, microwave power and amount of water used respectively. The extraction times tested were 60, 80, 100, 120, and 140 minutes.
at 210:10 water to sample ratio (mL/g) and power of 700 watts. As extraction time increased from 60 minutes to 120 minutes, the oil yield also increased with the optimum yield at 39 %. From 120 minutes to 140 minutes, the yield obtained was stagnant which indicated the extraction reached equilibrium. Microwave energy work selectively and diffuse very well within polar molecules such as water. Water thus works well as an extraction solvent replacing hazardous organic solvents such as hexane and petroleum ether often used in extraction of oil. Microwave energy emitted as waves work well with water rather than hexane.

Energy emitted during extraction process help in rupturing the cell wall of the seed sample thus releasing the oil. The oil yield using microwave extraction was lower compared to yield obtained using Soxhlet apparatus which was 48.16 % [2]. However the yield obtained in this study could be considered as high when compared to the oil yields obtained using several extraction methods ranging from 20-60 % [4]. Several factors such as climate, storage and variety influence the oil yield of Jatropha curcas.

### Table 1. Effect of extraction time on Jatropha oil yield.

| Time (minutes) | Yield (%) |
|---------------|-----------|
| 60            | 9.2       |
| 80            | 12.6      |
| 100           | 25.5      |
| 120           | 38.9      |
| 140           | 38.8      |

3.2. Effect of extraction power on Jatropha oil yield

Jatropha oil was extracted at various power (watt) ranging from 200, 300, 400, 500, 600 and 700 watts at 120 minutes extraction time and 210:10 g water to sample ratio (mL:g). The maximum power supply was 700 watts. The oil yield for each watt power used at 200, 300, 400, 500, 600 and 700 watt were 5.2, 11.3, 18.4, 28.6, 33.6, and 38.7 % respectively which showed an increased in yield as power was increased. The extraction technique using microwave technique lies in its ability to expose sample to heat caused by microwave field [5]. The heating ability by this technique is efficient and fast compared to conventional extraction method where sample was heated by conduction [6].

### Table 2. Effect of extraction power on Jatropha oil yield.

| Time (minutes) | Yield (%) |
|---------------|-----------|
| 200           | 5.2       |
| 300           | 11.3      |
| 400           | 18.4      |
| 500           | 28.6      |
| 600           | 33.6      |
| 700           | 38.7      |

3.3 Effect of water volume on Jatropha oil yield

When extracting oil from Jatropha seeds, another important parameter to investigate was volume of water per sample. Weight of sample used was 10 g and extraction was carried out at a constant extraction time of 120 minutes and a power of 700 watts. The volume of water used was determined at 70, 100, 130, 160, 190 and 210 mL. There was an increase in yield from 70 mL to 160 mL and yield was stagnant from 160 to 210 mL of water insignificant differences between the values. Thus it can be concluded that volume of water of 190 mL gives highest yield of bio-oil. Water plays
an important role to keep the sample moist. The dipole rotation of water when exposed to microwave energy will rotate quickly and produce heat. This process resulted in cell walls to expand and rupture thus releasing essential oil into the solvents. Sometimes, dry samples are rehydrated before extraction to encourage localized heating to take place. Moreover, moisture content is crucial in MAE because water superheats and promotes solute to be emancipated into solvents.

### Table 3. Effect of water volume on *Jatropha* oil yield.

| Water volume (ml) | Yield (%) |
|-------------------|-----------|
| 70                | 9.1       |
| 100               | 15.8      |
| 130               | 27.8      |
| 160               | 37.7      |
| 190               | 37.9      |
| 210               | 37.6      |

#### 3.4. Physico-chemical characterization of bio-oil

*Jatropha curcas* oil was tested for its oil quality and fatty acid composition and the results obtained are as shown in table 4. The acid value, free fatty acid, iodine value, peroxide value and saponification value were 2.8 mg KOH·g⁻¹, 1.7, 102.1 mg/g, 2.23 m Eq/kg and 190.4 mg/g respectively. From this study the acid value was comparable to previous studies by several authors [7, 8, 9].

### Table 4. Physicochemical properties of *Jatropha* oil yield.

| Characteristic                  | Value  |
|---------------------------------|--------|
| Acid value (mgKOH·g⁻¹)          | 2.8    |
| Free fatty acid                 | 1.7    |
| Iodine value (mg/g)             | 102.1  |
| Peroxide value (mEq/kg)         | 2.2    |
| Saponification value (mg/g)     | 190.4  |

The extracted oil showed great quality in terms of its acid value as it was lower than the permissible value which is 10. Acid value measures the existence of oxidation product that is corrosive when used in engines [10]. High unsaturation of fatty acid will give high iodine value. There are two types of oil which is drying and semidrying. Iodine value of oil higher than 125 mg/g will be categorized as drying while iodine value between 110–140 mg/g categorised as semidrying of oils. The saponification value was higher than that obtained from *Bassia longifolia* 185.5 mg KOH/g, *Indonesia Jatropha* oil 183.2 mg KOH/g and *Indian Jatropha* oil 156.2 mg KOH/g. The major composition of fatty acid was determined from gas chromatography (GC) technique and the unsaturated fatty acid content was 72.9 % followed by saturated fatty acid content of 24%. The unsaturated fatty acid comprised oleic acid 41.7 % and linoleic acid 30.8%. The saturated fatty acid was palmitic acid 17.1 % and stearic 6.9 %. The fatty acid compositions is as shown in table 5.
Table 5. Fatty acid composition of *Jatropha* oil yield.

| Fatty acid      | Value |
|-----------------|-------|
| Oleic acid      | 41.6  |
| Linoleic acid   | 30.8  |
| Palmitic acid   | 17.1  |
| Stearic acid    | 6.9   |
| Saturated       | 24.0  |
| Fatty Acid      | 72.9  |

3.5 Effect of calcined seashell catalyst in the pyrolysis process

In a series of pyrolysis, the experiment was determined at catalyst biomass loading of 0 wt. %, 5 wt. %, 10 wt. %, 15 wt. % and 20 wt. %, constant nitrogen flow rate of 250 cc/min, pyrolysis temperature of 638 °C, heating rate at 10 °C /min and particle size of 500-1000 µm. Figure 3 shows the effect of catalyst on oil yield. Bio-oil yield for non-catalytic extraction was 43.8 %. The optimum bio-oil yield was 44.5 % achieved at 5 % of catalyst loading. However, bio-oil yield was slightly reduced from 43.7 to 42.1 % with addition of 10 to 20 % catalyst. According to Rohim *et al.* [3] it could be due to the agglomeration of active CaO phase and the covering of basic sites by excess CaO, thus resulting in lower oil yield.

![Figure 3. Effect of the amount of catalyst and bio-oil yield.](image)
Bio-oil yield with addition of catalyst induced extraction increased from 43.8 % to 44.6 % as compared to the non-catalytic process. Therefore addition of catalyst enhanced the quality and yield of bio-oil products but production of syngas was reduced by 21.7 %.

3.6. Physicochemical characterization of bio-oil

3.6.1 Viscosity and pH. The properties of bio-oil produced from EFB are given in table 6. The optimization of bio-oil under optimized condition was used for bio-oil characterization. The pH value of bio-oil at room temperature is noticeably acidic with a pH of 3.5. This finding is in agreement with Sukiran [11] in which the presence of diluted water and volatile acids, such as acetic and formic acid, resulted in low pH of bio-oil. The pH value determined by catalytic pyrolysis of bio-oil was higher at pH 4.5 as compared to non-catalytic extraction of pH 3.5 (table 6). Bio-oil obtained by catalytic technique was less acidic therefore enhanced quality. The presence of acid in bio-oil is one of the main factors for corrosivity to materials in storage and application processes [12].

| Properties   | Non-catalytic bio-oil | Catalytic bio-oil |
|--------------|-----------------------|-------------------|
| Viscosity(cP)| 20.5                  | 37.7              |
| pH           | 3.5                   | 4.3               |

Bio-oil viscosity was 20.5 cP for non-catalytic extraction of bio-oil and 37.7 cP for catalytic bio-oil extraction. Viscosity is related to the ability of the liquid to flow. The bio-oil obtained from this study was low in viscosity. This could be due to high value of water content, causing it to be less viscous. The presence of water content in bio-oil is mainly due to reaction from the lignin present in the raw material which was approximately 53.4 % [13].

4. Conclusion

The maximum oil yield was obtained with optimum extraction parameters of extraction time of 120 minutes, microwave power of 700 watts and 190ml of water used. The bio-oil yield extracted using MAE showed good quality based on its physico-chemical and fatty acid composition. Water used as an extractant solvent is clean, abundant, readily available and importantly non-hazardous to human health, living things and atmosphere. It is a fast extraction technique and enhanced quality of bio-oil. Similarly, the use of waste seashell as a biocatalyst improved bio-oil extraction from biomass waste such as EFB. This natural biocatalyst enhanced yield and quality of bio-oil. The extraction techniques and parameters used in this study showed potential to be explored and developed as a green technology to reduce environmental pollution. This process is also cost effective since water is cheaper than chemical solvent. Natural catalyst from waste seashells is also environment friendly and cost effective compared to chemically based calcium oxide.

5. References

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