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Jatropha curcas L. oil extracted by switchable solvent *N*, *N*-dimethylcyclohexylamine for biodiesel production☆

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ABSTRACT

Biodiesel, which is a renewable and environmentally friendly fuel, has been studied widely to help remedy increasing environmental problems. One of the key processes of biodiesel production is oil extraction from oilseed materials. Switchable solvents can reversibly change from molecular to ionic solvents under atmospheric CO₂, and can be used for oil extraction. *N*, *N*-dimethylcyclohexylamine (DMCHA), a switchable solvent, was used to extract oil from *Jatropha curcas* L. oil seeds to produce biodiesel. The appropriate extraction conditions were: 1:2 ratio of seed mass to DMCHA volume, 0.3–1 mm particle size, 200 r·min⁻¹ agitation speed, 60 min extraction time, and 30 °C extraction temperature. The extraction ratio was about 83%. This solvent extracted the oil more efficiently than hexane, and is much less volatile. By bubbling CO₂ under 1 atm and 25 °C for 5 h, the oil was separated, and DMCHA was recovered after releasing CO₂ by bubbling N₂ under 1 atm and 60 °C for 2 h. The residual solvent content in oil was about 1.7%. Selectivity of DMCHA was evaluated by detecting the protein and sugar content in oil. Using the oil with residual solvent to conduct transesterification process, the oil conversion ratio was approximately 99.5%.

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1. Introduction

The rapid consumption of fossil fuels and the negative effects of greenhouse gas emissions on global climate change are bringing attention to bio-resources, such as biodiesel [1], a renewable, biodegradable, and environmentally friendly fuel [2] that can be used in current compression ignition engine without any mechanical changes [3]. The process of biodiesel production consists of three parts: oil extraction, transesterification, and the separation and purification of the product. The cost of feedstock accounts for 75%–80% of the total cost of biodiesel production. Getting a higher oil extraction ratio and reducing the energy consumption of the extraction process can efficiently reduce the total cost of biodiesel production.

Conventional oil extraction methods include mechanical pressing (including screw-press and cold pressing), supercritical fluid extraction, and traditional solvent extraction. Mechanical extraction using a high pressure screw press is a well commercialized method that is ideal for edible oil production since no organic solvent is used during the process [4]. Abu-Arabi *et al.* studied the extraction efficiency of jojoba oil via pressing in which about 70% of the oil was extracted after a single

pressing under 34.5 MPa [5]. The high pressure results in high energy consumption. Martinez *et al.* studied the effect of moisture on screw-press extraction. The pretreatment consisted of a number of unit operations such as cleaning, cracking, cooking, drying or moistening to achieve an optimal moisture content [4]. Screw press extraction can be problematic due to its low yield and productivity, high energy consumption, and a complicated pretreatment and extraction process.

Supercritical fluid extraction (SFE) using carbon dioxide is a popular technique for oil extraction due to its high extraction efficiency, short extraction time, lower refining requirement, and absence of other chemicals or contamination in the extracted oils [6]. Typically, the operational pressure of oil extraction by SC-CO₂ is above 20 MPa [7–9]. However, the high cost of instruments and operation confines its industrial application.

The solvent extraction method was introduced in the United States in the 1930s [10] when hexane was used to extract soybean oil. This method provided an economically high yield [11]. In this method, oil is leached out and separated by distilling and recycling the hexane, which may result in solvent loss and environmental pollution due to the low boiling point of hexane. At the same time, the distillation is an energy intensive process [12], which results in high energy consumption.

In order to obtain higher oil extraction efficiency and get an effective solution to environmental pollution caused by solvent evaporation and high energy consumption, a switchable solvent seems to be an appropriate option. Switchable solvents are liquids whose

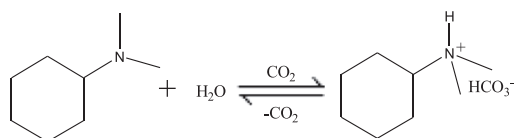
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polarity or hydrophilicity can be reversibly switched from one form to another in the presence or absence of CO₂ [13]. Switchable solvents include switchable polarity solvent (SPS) like DBU (1, 8-diazabicyclo- [5.4.0]-undec-7-ene) and switchable hydrophilicity solvent (SHS) like *N,N*-dimethylcyclohexylamine (DMCHA). Both of them are non-flammable and non-volatile. They are promising solvents for oil extraction.

Switchable solvent was recently used to efficiently extract oil from soybeans and microalgae [14,15]. By using switchable solvents in the oil extraction, the separation is accomplished through phase change. It avoids distillation or volatilization in the solvent recovery. The solvent itself is non-polar and was used to leach the oil out from oil seeds. Then, it was separated from the oil by absorbing CO₂, in which it reacted with CO₂ in the presence of alcohol or water to form polar or hydrophilic carbonates. The solvent was recycled after releasing CO₂. It converts to the original non-polar or hydrophobic forms. The switching equation of DMCHA is shown as follows.



There are studies about oil extraction with DBU and/or alcohols. Jessop *et al.* [14] investigated soybean oil extraction and subsequent solvent removal from the oil with DBU. The oil yield by DBU and ethanol extraction were about 50% and 75% of total oil, however, DBU/ethanol mixture had only 45% of oil yield because of transesterification. Samori *et al.* used DBU/alcohol SPS to extract lipids from algae [15]. DBU/1-octanol was found to be superior to the conventional extraction with hexane from both freeze-dried and wet algae samples. In order to avoid the formation of DBU-bicarbonate, a further step to remove the residual water was necessary before treating the SPS with CO₂. So the mixture of DBU/alcohol is not suitable for oil extraction, because the separation of solvents was difficult when they were used for the wet sample. The water contained in the seed severely influences extraction due to the formation of strong hydrogen bonds with the solvent in the polarity switching process. Meanwhile, the co-existence of DBU/alcohol results in the alcoholysis of oil to form esters.

Switchable hydrophilicity solvent DMCHA could be used for the aqueous sample because the switching process occurs with water. From Jessop's [16] work, the SHS DMCHA extracted up to 22 wt% crude lipid relative to the freeze-dried microalgae cell (2% water content) mass. The phase change was successful and 83% of DMCHA was recovered after CO₂ stripping. Samori *et al.* [17] studied the lipid extraction process from three kinds of algae cultures (80% water content) using DMCHA. The extraction yields were higher than those of the typical hot extraction procedure with CHCl₃/MeOH. It can be concluded that DMCHA works well with crude oilseeds that normally contain some moisture.

However, in the system of oil extraction by DMCHA, some lipid remained in the recovered solvent and residual solvent in the extracted oil could affect their further application.

Jatropha curcas L., a drought-resistant shrub or tree, is widely distributed in the wild or semi-cultivated areas in Central and South America, Africa, India and South East Asia. Its decorticated seeds contain 40–60% oil, which is inedible oil due to the presence of toxic phorbol ester [18]. But it can be used in many areas such as lighting, as a lubricant for making soaps, and most importantly, used to produce biodiesel [17]. It is a very suitable feedstock for biodiesel production. The product presents good properties by transesterification from *J. curcas* L. oil [19,20].

The oil contained in *J. curcas* L. seeds is stored as oil bodies in cells, surrounded by cell walls. Cell breakage can accelerate the mass transfer in the leaching process. It can be done by mechanical pressing assisted with ultrasound [21] and enzymatic conversion [22]. Oil leaks out from broken cells and dissolves in solvent.

In this work, the switchable solvent, DMCHA, was used to extract *J. curcas* L. oil from crushed *Jatropha curcas* seeds to investigate the efficiency and feasibility of its use in biodiesel production. In the process, oil is extracted by the solvent DMCHA and separated by bubbling CO₂ into the system in the presence of water. The solvent is recovered through the release of CO₂. The whole process was studied. The relative technical parameters, including extraction time, ratio of seed mass to solvent, oil seed size, agitation speed, and extraction temperature were systematically studied to get a better understanding of this extraction system. Compositions of the extracted oil and the recovered solvent were also measured. The extracted oil was investigated for the production of biodiesel.

2. Materials and Methods

2.1. Materials

The *J. curcas* L. seeds were collected from Panzhihua area, Sichuan Province, southwest China. The seeds were decorticated, crushed and sieved. *N,N*-dimethylcyclohexylamine (industrial grade >99%) with water content <0.14% (detected by the Karl Fischer method) was purchased from Shanghai Beihe Chemical Co. Ltd. Hexane (AR grade) was purchased from Chengdu Kelong Chemical Co. Ltd. The properties of the solvents and oil are listed in Table 1.

Table 1
Properties of the solvents and oil

Properties	Hexane	DMCHA	Oil ^①
Density ^② /g·ml ⁻¹	0.67	0.849	0.9 ± 0.1
Boiling point ^② /°C	68.5 ± 3.0	162.0 ± 8.0	818.7 ± 55.0
Vapor pressure ^② /mmHg	150.9 ± 0.1	2.2 ± 0.3	0.0 ± 3.0
Polarizability ^② ×10 ²⁴ /cm ³	11.8 ± 0.5	16.2 ± 0.5	107.7 ± 0.5
Dielectric constant (relative permittivity) ^③	1.89	2.86	3.109
Dipole moments ^③ /D	0	0.76	Not found

^① Triolein was used to represent oil.

^② Data from <http://www.chemspider.com/> (last accessed on December 17, 2015), 1 mmHg=133.322Pa.

^③ Data from the 82nd Edition of the *CRC Handbook of Chemistry and Physics*.

2.2. The process of biodiesel production from *J. curcas* L. oil extracted by DMCHA

2.2.1. The process chart

Fig. 1 shows the oil extraction and solvent recovery process.

2.2.2. Oil extraction by Soxhlet method and DMCHA method

To determine the total oil content (x_0 , %) of the *J. curcas* L. seeds (m_0 , g), 20 g of crushed seeds were extracted in a Soxhlet extractor at 80 °C for 6 h by using 200 ml hexane. After extraction, the hexane was removed by vacuum evaporation. The mass (m_1 , g) of oil could then be obtained. The oil content was (60.0 ± 0.5) wt%, estimated by Eq. (1).

$$x_0 = \frac{m_1}{m_0} \times 100\% \quad (1)$$

20 g of *J. curcas* L. seeds were extracted by DMCHA inside a 250 ml three-necked flask with a reflux condenser, and the extraction was investigated under different conditions. After extraction, the mixture was filtered under a vacuum with Whatman#1 filter paper. The cake was dried at 50 °C and then weighed (m_2). The mass (m_3 , g) of oil in the cake could be obtained by the Soxhlet method. The oil content of residual solids (O CRS) (x_1 , %) was determined by Eq. (2). Each

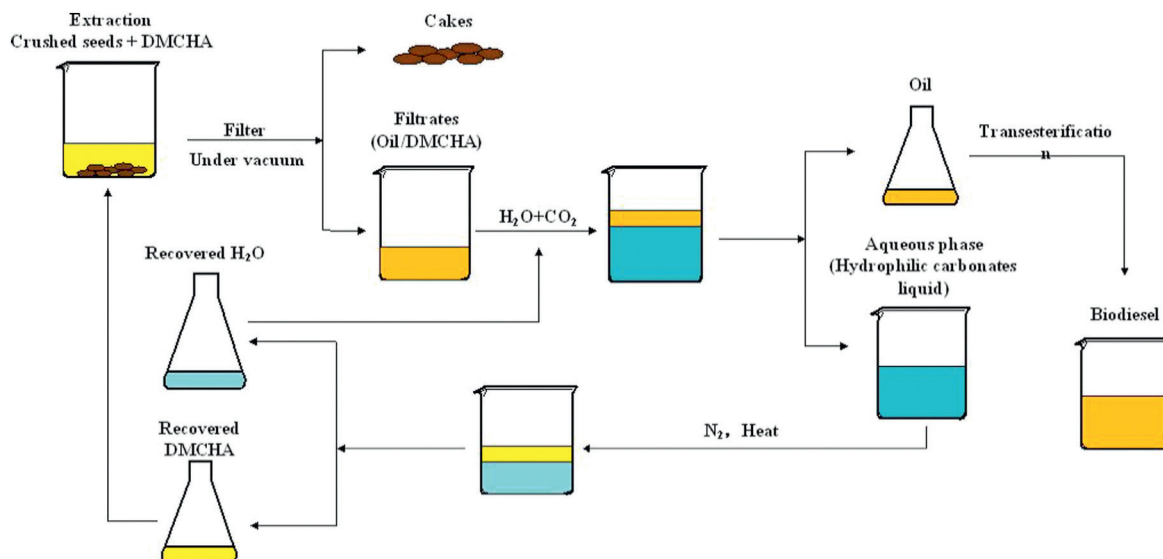


Fig. 1. The process of oil extraction and solvent recovery.

extraction process under different conditions was performed in duplicate.

$$x_1 = \frac{m_3}{m_2} \times 100\%. \quad (2)$$

The oil extraction ratio by DMCHA was calculated as Eq. (3).

$$\text{Extraction ratio} = \frac{m_1 - m_3}{m_1} \times 100\%. \quad (3)$$

2.2.3. Recovery of oil and solvent

Water was added to the filtrates containing solvent and oil, then CO₂ gas was bubbled through the liquid in a three-necked flask with a reflux condenser. The bubbling operation was conducted under 1 atm and 25 °C for 5 h. By absorbing CO₂, the solvent DMCHA and water reacted to form an aqueous layer in the bottom of the flask. Oil separated to form an oily phase in the upper layer. After overnight settling, the oily layer was recovered and its mass was measured.

The lower layer was the aqueous solution containing water. After measuring the mass, it was bubbled with N₂ in the flask under 1 atm and 60 °C for 2 h to release CO₂. The solvent DMCHA switched back to its original form, which is almost immiscible with water, separated from aqueous phase, formed the upper layer, and was recovered.

2.2.4. Production of biodiesel

The extracted oil was used to conduct transesterification experiments. Before the transesterification process, the free fatty acid in the oil was neutralized by KOH after the acid value was determined following the methods described in the National Standard of PRC GB/T 5530-2005. After that the oil was washed with water several times and the water in the oil was removed by anhydrous magnesium sulfate.

The transesterification reaction was conducted in a three-necked flask with a stirring rotor and a condenser. The conditions were: 1 wt% KOH of oil mass, 6:1 molar ratio of methanol to oil, and in a water bath at 64 °C for 1 h. As a comparison, the same amount of oil after pretreatment without adding catalyst for transesterification was conducted under the same condition.

Transesterification product was placed in a separatory funnel, washed three times with hot water, and the aqueous phases were combined. The glycerol content in aqueous phase was measured by sodium periodate oxidation method according to Chinese standard GB/T 13216-

2008, and the glycerol conversion ratio was calculated, which could be used to represent oil conversion ratio. The upper layer was methyl ester phase, which was dried overnight by anhydrous sodium sulfate and the components were analyzed by gas chromatography. Some of the properties of methyl ester phase were measured according to Chinese standard GB/T 20828-2014.

2.3. Analysis of oil and recovered solvent

The sugar and protein content in oil extracted by DMCHA are not easy to detect directly. They can be obtained by subtracting the content in the meal from the content in the raw materials. The residual solvent in the recovered oil was analyzed by GC, and the residual oil in the recovered solvent was also measured. The water content and acid value of the recovered oil and solvent were also measured. All the analytical methods are shown in Table 2. Except the GC method and phosphate-vanillin staining method [23], other methods are from National Standard of PRC, so the corresponding national standards are also included in the table.

The sugar and protein content in the oil can be calculated by Eqs. (4) and (5).

$$\text{Sugar content of oil} = \frac{m_0 a_0 - m_2 a_1}{m_0 x_0 - m_2 x_1} \quad (4)$$

$$\text{Protein content of oil} = \frac{m_0 b_0 - m_2 b_1}{m_0 x_0 - m_2 x_1} \quad (5)$$

a_0 : sugar content of raw material a_1 : sugar content of meal m_0 : mass of raw material

m_2 : mass of meal x_0 : oil content of raw material x_1 : oil content of meal

b_0 : protein content of raw material b_1 : protein content of meal.

The residual solvent content was analyzed using GC by a modified ASTM standard D 6584. The operating conditions were: inlet heater temperature: 380 °C; split ratio: 20:1; initial pressure: 0.05 MPa; detector temperature: 385 °C; air flow rate: 400 ml·min⁻¹; flow rate of hydrogen: 45 ml·min⁻¹; N₂ flow rate: 25 ml·min⁻¹; the oven temperature: 50 °C maintained 1 min; 10 °C·min⁻¹ to 70 °C; 100 °C·min⁻¹ to 300 °C; and 20 °C·min⁻¹ to 380 °C, maintained 5 min. Comparing chromatographic peak areas with a standard curve obtained by detecting a series of different concentrations of DMCHA, the amount of residual solvent in the oil was obtained.

Table 2

Analytical methods of each composition

Composition	Sugar	Protein	Residual solvent	Residual oil	Water	Acid number
Method	Phenol-sulfuric acid method	Kjeldahl method	GC	Phosphate-vanillin staining	Karl Fischer	
National standard of PRC	GB/T 15672-2009	GB/T 14489.2-2008			GB/T 26626-2011	GB/T 5530-2005

3. Results and Discussion

3.1. Parameters of the oil extraction process

In order to get an appropriate extraction condition, the effects of extraction time, solvent volume, particle size, extraction temperature, and extraction agitation on extraction efficiency were studied, and the oil extraction efficiency of DMCHA and hexane was compared.

3.1.1. Effect of time on extraction efficiency

The effect of leaching time on the oil extraction ratio was studied. As shown in Fig. 2, the extraction ratio increased with leaching time in the initial period, then tended to a steady value. In the first 10 min, about 76% of oil was extracted and the maximum extraction ratio, nearly 83%, was obtained in 60 min. Meanwhile, the oil content of the residual solid dramatically decreased from the original 60% to 25% in the first 10 min. The result was similar to Qian *et al.*'s [24] work, in which *J. curcas* L. oil was extracted via two-phase solvent extraction. In that work, nearly 90% of the oil was extracted in the first 10 min, and only 8% was extracted in the next 50 min. Fig. 2 shows the oil content of the residual solid was about 20% after 6 h of extraction. The results are explained by a standard equilibrium mass transfer argument. When the oil concentration in the solvent increased, the oil diffusion rate decreased, and the oil content in the two phases reached an equilibrium value that prevented further oil dissolution into the solvent phase.

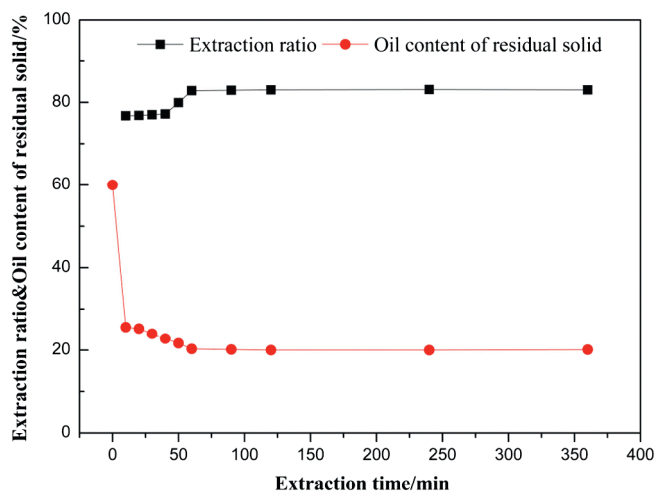


Fig. 2. Effect of time on extraction efficiency (extraction condition: 1:2 ratio of seed mass to DMCHA volume, 0.3–1 mm particle size, 200 r·min⁻¹ agitation speed, and 30 °C extraction temperature.)

3.1.2. Effect of solvent volume on extraction efficiency

Extraction with solvent is a dissolving process, and the extraction ratio is directly associated with the solvent volume. The effect of solvent volume on extraction efficiency is shown in Fig. 3. The extraction ratio increased with solvent volume, but increased slowly after the ratio of seed mass to solvent volume went above 1:2 (g·ml⁻¹), at which the extraction ratio was 83% and the OCRS was 20%. The extraction ratio was only about 3.5% higher, even though the ratio of seed mass to solvent

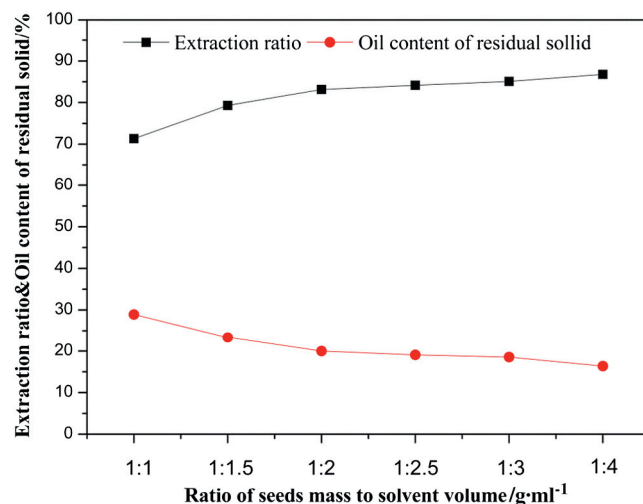


Fig. 3. Effect of solvent volume on extraction efficiency (extraction condition: 0.3–1 mm particle size, 200 r·min⁻¹ agitation speed, 60 min extraction time, and 30 °C extraction temperature.)

volume reached 1:4. It can be speculated that the content of extracted oil only increased a little with the increased amount of solvent, and the residual oil was hardly extracted due to the low concentration difference. When the ratio of seed mass to solvent volume was under 1:2, the agitation was ineffective, which resulted in low extraction efficiency.

To figure out if a 1:2 ratio of seed mass to solvent volume can dissolve oil, intersolubility between *J. curcas* L. oil and DMCHA was measured by turbidimetric analysis using the titration method under isothermal conditions. The result indicated that *J. curcas* L. seed oil and DMCHA were completely miscible. So, the ratio of seed mass to solvent volume was set at 1:2, which was enough to dissolve the oil, and used in further experiments.

3.1.3. Effect of particle size on extraction efficiency

Particle size of the crushed seeds may influence the extraction efficiency. The crushed seeds were sieved and 3 sizes of <0.3 mm, 0.3–1 mm and 1–2 mm of seed particles were tested in extraction under the same conditions. The effect of particle size on extraction efficiency is shown in Fig. 4. The results showed nearly the same extraction ratio. About 80% was obtained with the 3 particle sizes, and the biggest difference observed was only about 3%. When the decorticated *J. curcas* L. seeds were extracted without crushing (particle size was about 5–10 mm), the extraction ratio was only 8%. The low extraction ratio is probably due to the dense structure of the seeds and the intact cell walls reduced or prevented the solvent diffusion into the cells [25]. After *J. curcas* L. seeds were crushed, some cell walls were broken, as indicated by a small amount of oil that came out of the cracked solids. The effect of particle size on oil extraction was insensitive after the crushing process. DMCHA can dissolve the oil quickly. The key factor during extraction may be the integrity of the cell walls. Particle sizes between 0.3 and 1 mm were used in other experiments.

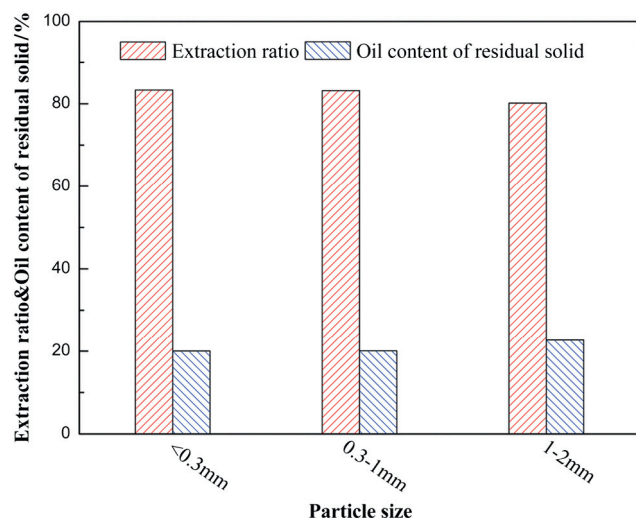


Fig. 4. Effect of particle size on extraction efficiency (Extraction condition: 1:2 ratio of seed mass to DMCHA volume, $200 \text{ r} \cdot \text{min}^{-1}$ agitation speed, 60 min extraction time, and 30°C extraction temperature.)

3.1.4. Effect of extraction temperature and extraction agitation on extraction efficiency

The effects of temperature and agitation were studied. Extraction experiments at different temperatures were tested under the same conditions. The effect of extraction temperature on extraction efficiency is shown in Fig. 5. Results showed the extraction ratios at 30°C and 50°C were almost the same; about 83%, and both were about 5% higher than that at 10°C , which was about 78%. This indicates that a high temperature can accelerate the oil dissolution process to some extent, while a further increase in temperature has little effect on the extraction ratio and OCRS. At room temperature, the oil can be dissolved well in DMCHA.

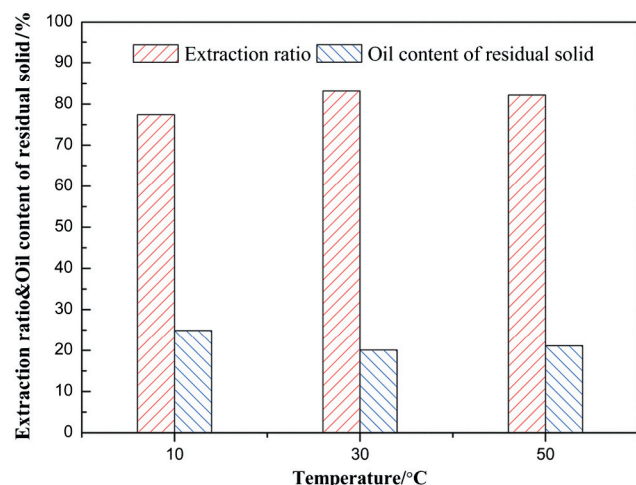


Fig. 5. Effect of extraction temperature on extraction efficiency (extraction condition: 1:2 ratio of seed mass to DMCHA volume, 0.3–1 mm particle size, $200 \text{ r} \cdot \text{min}^{-1}$ agitation speed, 60 min extraction time.)

Fig. 6 shows that the extraction ratio was insensitive to the agitation speed, in which the extraction ratio was about 83% and the oil content of the residual solid was 20%. The result was similar to the result of the extraction temperature experiments.

To get more information about the effects of particle size and agitation speed on the extraction process, solids crushed for two different lengths of time were extracted at different agitation speeds. The solids were the same particle size; 0.3–1 mm. As Table 3 shows, when the crushing time was 10 s, the extraction ratio was clearly sensitive to

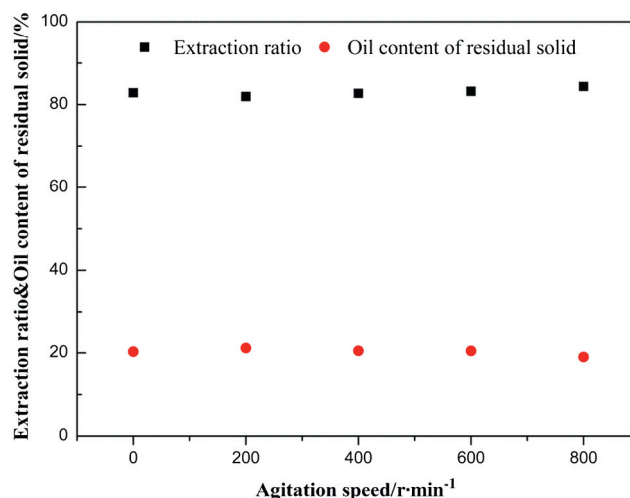


Fig. 6. Effect of agitation speed on extraction efficiency (extraction condition: 1:2 ratio of seed mass to DMCHA volume, 0.3–1 mm particle size, 60 min extraction time, and 30°C extraction temperature.)

Table 3

Effect of agitation under different crushing times

Crushing time/s	Agitation speed/ $\text{r} \cdot \text{min}^{-1}$	Extraction ratio/%	Oil content of residual solid/%
10	0	67.2 ± 0.1	33.0 ± 0.1
	400	76.4 ± 0.1	26.1 ± 0.1
120	0	82.8 ± 0.1	20.3 ± 0.1
	400	82.7 ± 0.1	20.5 ± 0.1

the agitation speed, but the extraction ratio was not sensitive to the agitation speed when the crushing time was 120 s. From their outward appearance, the solids were oilier when the seeds were crushed for 120 s rather than 10 s. That may indicate that more cell walls were broken during the longer crushing time, resulting in more oil being released into the cracks of the particles. The extraction efficiency can be increased by the crushing process significantly, and is insensitive to agitation. This result further verifies that breaking the cell walls is the key to the extraction process.

3.2. Comparison of different solvents for oil extraction

Hexane is usually used for oil extraction by counter-current flow extraction, and has proved to efficiently extract plant seed oil. The efficiency of DMCHA and hexane after batch extraction process was compared under the same conditions. Table 4 shows that the oil extraction ratio with DMCHA was nearly 16% higher than hexane, and the oil content of the residual solid was lower. Table 1 shows that the dielectric constants of DMCHA and oil are close to each other, and are both higher than hexane, which means that the polarity of DMCHA and oil are closer to each other than to hexane. The oil is expected to be more soluble in DMCHA. Therefore, the DMCHA showed higher extraction efficiency

Table 4

Comparison of DMCHA and hexane for oil extraction

Solvent	Hexane	DMCHA
Extraction ratio/%	66.7 ± 0.1	83.1 ± 0.1
OCRs/%	27.7 ± 0.1	20.0 ± 0.2
Water content/wt%	<0.2	2.6 ± 0.1
A.V./mg KOH $\cdot \text{g}^{-1}$	6.0 ± 0.1	2.2 ± 0.1
Sugar content in extracted oil/wt%	3.5 ± 0.1	0.8 ± 0.1
Protein content in extracted oil/wt%	3.7 ± 0.1	2.3 ± 0.2
Residual solvent content in extracted oil/wt%	–	1.7 ± 0.2

than hexane. DMCHA is also better for extraction because it is non-flammable and non-volatile (due to low vapor pressure, as shown in Table 1). Table 4 shows two important properties of extracted oil; the water content was about 2.6%, but can be dried below 0.1% by anhydrous magnesium sulfate and the acid number was about $2.2 \text{ mg KOH} \cdot \text{g}^{-1}$, which was lower than the oil extracted by hexane. The low acid number in the oil extracted by DMCHA is probably due to the acid–base reaction between fatty acid and DMCHA.

The sugar, protein and residual solvent content of the oils extracted by hexane and DMCHA were also measured and compared in Table 4. The results show that the selectivity of DMCHA is better than the conventional hexane oil extraction solvent.

3.3. Recovery of oil and solvent

When the extraction conditions were 20 g of solids, 0.3–1 mm particle size, 40 ml (about 34 g) of DMCHA, $200 \text{ r} \cdot \text{min}^{-1}$ agitation speed, 60 min of extraction time, and 30°C extraction temp, 9.6 g of oil was recovered by bubbling CO_2 through the filtrate solution mixed with water. Bubbling CO_2 caused the DMCHA to switch from non-polar to polar and therefore separate from the oil phase. This oil recovery was 95.0% of the result calculated by the total oil content minus the oil content of residual solids. Fig. 7 shows the material balance results of the whole extraction process. As can be seen, the solvent losses are mainly in the cake and the aqueous solution of recovered water. Since the solution can be directly returned to the system, recovering the solvent in the cake is necessary to reduce solvent loss and cost. Washing the cake with carbonated water and reusing the water to the oil recovering system may also be an available access.

The more difficult process was the SHS solvent (DMCHA) recovery. A phase separation of DMCHA from water was forced by bubbling N_2 at 60°C through the remaining filtrate solution after the oil was removed. After bubbling N_2 for about 120 min, a crude solvent phase was obtained, and about 64.8% of the original solvent was recovered. The crude solvent contained about 9.8% water, which could be removed by anhydrous magnesium sulfate before the IR detection. The residual

oil content of the recovered solvent was approximately 3.1%. The distributions of oil and DMCHA in the system are demonstrated in Tables 5 and 6. As Fig. 8 shows, the IR spectra of the recovered solvent and the fresh DMCHA are in close agreement.

Table 5

The distribution of oil in the extraction system

In seeds	Recovered oil	In cakes	In recovered DMCHA
12.2 g	9.4 g 77.1%	2.1 g 17.2%	0.7 g 5.7%

Table 6

The distributions of DMCHA in the extraction system

Fresh solvent	Recovered solvents	In cakes	In recovered water	In recovered oil	Solvent loss
34.1 g	22.1 g 64.8%	6.6 g 19.4%	4.0 g 11.7%	0.2 g 0.6%	1.2 g 3.5%

3.4. Reuse of recovered solvent

The recovered solvent was used to extract oil under the appropriate conditions: 1:2 ratio of seed mass to DMCHA volume, 0.3–1 mm particle size, $200 \text{ r} \cdot \text{min}^{-1}$ agitation speed, 60 min extraction time, and a 30°C extraction temperature. The extraction ratio was about 77%, which is 6% lower than that of the fresh solvent. The residual solvent content in the recovered oil was about 1.7% after bubbling CO_2 for 5 h, which was the same as the oil extracted by the fresh solvent. The acid value of the oil is about $2.2 \text{ mg} \cdot \text{g}^{-1}$, and the water content of the oil is about 2.6%, which is also the same as the oil extracted by fresh solvent.

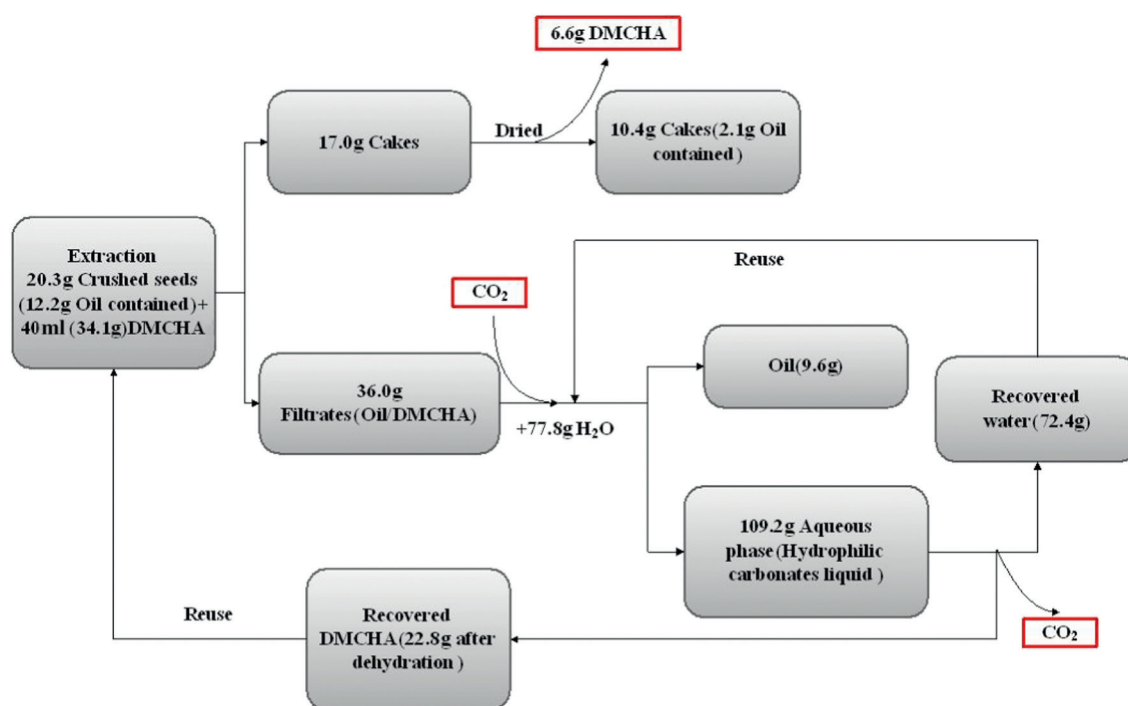


Fig. 7. The material balance results of the whole extraction process.

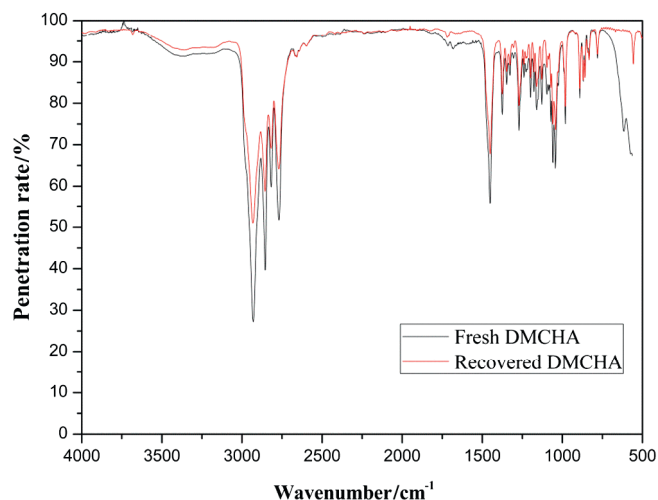


Fig. 8. IR spectra of recovered and fresh DMCHA.

So, the recovered DMCHA with 3.1% residual oil and 9.8% water can be reused normally with a lower oil extraction ratio than that of fresh DMCHA.

3.5. Production of biodiesel

The *J. curcas* L. oil extracted by DMCHA, containing about 1.7% residual solvents, was used to conduct the transesterification process. In the presence of KOH as catalyst, the conversion ratio of oil was ($99.5 \pm 0.1\%$) and the methyl ester content of the crude biodiesel was ($98.4 \pm 0.2\%$), which was in line with the requirement in Chinese standard GB/T 20828-2014, above 96.5%. Meanwhile, in the absence of a catalyst, the transesterification experiment resulted in a 0.8% conversion ratio of oil, and a 0.2% methyl ester content of the methyl ester phase. The results showed that DMCHA had little catalytic activity for the transesterification process, and the presence of residual solvent in the oil did have a small negative effect on the preparation of biodiesel, which should be studied deeply. Some properties of the crude product were measured, and the results are listed in Table 7.

4. Conclusions

Switchable solvent DMCHA was used to extract oil from *J. curcas* L. seeds with higher oil extraction efficiency and less volatility than hexane. By determining the sugar and protein content in the oil, DMCHA exhibited better selectivity than hexane in the oil extraction process. Broken cell walls are key to the extraction process, along with crushing time and the volume of the solvent. The extraction was insensitive to agitation, particle size and extraction temperature. As a result, the appropriate conditions in a batch extraction were: 1:2 ratio of seed mass to DMCHA volume, 0.3–1 mm particle size, $200 \text{ r} \cdot \text{min}^{-1}$ agitation speed, 60 min extraction time, and a 30°C extraction temperature. The extraction ratio was about 83%. More complete extraction would be obtained by counter-current extraction.

Table 7
Properties of the biodiesel production

	Acid value/ $\text{mg} \cdot \text{g}^{-1}$	Water content/%	Density/ $\text{kg} \cdot \text{m}^{-3}$	Viscosity/ $\text{mm}^3 \cdot \text{s}^{-1}$
Product	0.40 ± 0.10	<0.01	877.0 ± 0.5	4.5 ± 0.3
Chinese standard GB/T 20828-2014	≤ 0.50	≤ 0.05	820–900	1.9–6.0

The oil recovery by bubbling CO_2 was easily accomplished, while the solvent recovery ratio of 64.8% was not ideal at present experimental conditions. The solvent losses are mainly in the cake (19.4% of total solvent) and in an aqueous solution of recovered water (11.7% of total solvent), and there is also about 1.7 wt% residual solvent in the oil. Therefore, further work should focus on the process of oil and solvent recovery.

The oil extracted by DMCHA containing 1.7% solvent could be used to produce biodiesel with no difference in the conversion ratio of pure oil, and the methyl ester content of the crude biodiesel was 98.4%, which was in line with the requirement in Chinese standard GB/T 20828-2014, above 96.5%. Purification and application should be studied further in the future to get a better economical efficiency and a further knowledge about its use in diesel engines.

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