

Review

Jojoba oil: A state of the art review and future prospects

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ABSTRACT

Jojoba oil, which is derived from the extraction of Jojoba seed, has a peculiar molecular structure in comparison with the rest of conventional oils. Jojoba oil is formed by long monounsaturated esters whereas the rest of the oils are usually composed by triglycerides. This unconventional structure confers to Jojoba oil unique properties and characteristics that are very valuable for fine chemical industry and for the production of pharmaceuticals. In addition, Jojoba oil can be an excellent source of fatty acid alkyl esters or biodiesel after the transesterification process and the purification steps. This review presents general information about the production of Jojoba oil and its derivatives, its composition, oil extraction process and the applications of this oil when it is used directly or after chemical transformation as well as the possible purposes of Jojoba meal after extraction.

In addition, this paper contemplates the advantages and disadvantages of the use of homogeneous and heterogeneous catalysts for the Jojoba oil transesterification as well as different methods to obtain long monounsaturated alcohols, which have pharmaceutical applications, after being separated from biodiesel. The properties of the products derived from the transesterification of Jojoba oil are broadly discussed. Moreover, this review suggests future research opportunities such as a possible biorefinery using Jojoba oil as main raw material, supercritical methods and simultaneous extraction/reaction process which are fully discussed.

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1. Introduction

Joboba plant or *Simmondsia chinensis* is a desert-like perennial shrub, which is linked to the Buxaceae family [1], and it is the raw material necessary to obtain one-of-a-kind mixture of high-molecular weight monounsaturated esters [2] in the range of C_{34} to C_{50} . Joboba plant is native to the Sonoran desert and it is extremely tolerant to different environments. For example, Joboba might be cultivated at sea level and at 1500 m altitude [2], showing its versatility at completely different conditions. Joboba is mostly cultivated in arid and semi-desert zones such as different zones of the US, Israel, Mexico, India and South Africa [1,3]. Joboba plant oil yield is approximately 1818 kg/ha which is a little bit lower than *Jatropha* plant (1900–2500 kg/ha) but higher than *Camelina* (800–1200 kg/ha), which are three of the most important non-edible oils nowadays [3]. Thus, this plant has been used to prevent desertification in some parts of India [4] and therefore it could have a double role: economical and environmental. Many studies have been conducted in order to evaluate the resistance of the Joboba plant and it has been concluded that it tolerates tough conditions in terms of salinity, drought and heat [5]. Nevertheless, it is important to clarify that Joboba plant needs to improve its productivity when it is cultivated in the desert, under extreme conditions [5]. The height of Joboba plant is about 1 m and it is easily identified because of its thick, oval shape, bluish-green leaves and dark brown nut-like fruit [1,4,6].

Approximately, 50% of the seed's dry weight comprises Joboba oil [7], which is a mixture of monounsaturated C_{20} and C_{22} alcohols and acids where the double bond is situated at each side of the ester bond. Joboba oil composition is unique among the rest of the vegetable oils because of the almost complete absence of glycerine [8]. The particularities associated to this oil had been already known in the past when traditional cures were used to treat diseases such as sunburn, renal colic, chaffed skin, hair loss, headache, wounds and sorethroat [9]. In addition, Joboba oil is a unique source of straight monounsaturated alcohols such as 11-eicosenol, 13-docosenol and 15-tetracosenol, which they are classified as high-added value products. As it was mentioned, Joboba oil is formed by a mixture of esters, which confers to this peculiar oil many different properties such as suitability for sulfurization, high dielectric constant and ease to hydrogenate [1]. Thanks to these properties, Joboba oil could be used in many different industries [10] such as in cosmetics, pharmaceuticals, lubricants, heating insulators, foam control agents, high-pressure lubricants, heating oil, plasticizers, fire retardants, transformer oils and many more [2].

In order to achieve a panoramic view of the current situation of Joboba oil in terms of economy, extraction process, direct use and blending, transesterification process, product properties and future opportunities of this oil, the available literature has been thoroughly reviewed. This article will underline the current situation regarding Joboba oil in order to determine its future applications, waste generated from extraction process and its possible utilization.

2. Joboba oil and derivatives

From an economic point of view, the Joboba oil market is stronger than ever because their applications do not stop increasing, especially in the cosmetic and pharmaceutical industries [11]. Many researchers are realizing about the great difference between this unique oil and the rest of vegetable oils. Therefore, it is expected that worldwide Joboba oil production will grow sharply in the next few years as shown in Fig. 1 [5,12–14]. This fact can be confirmed taking into account the estimated Joboba oil demand in the world, that it is approximately 200,000 tons [15,16] which is enormously higher than the current production.

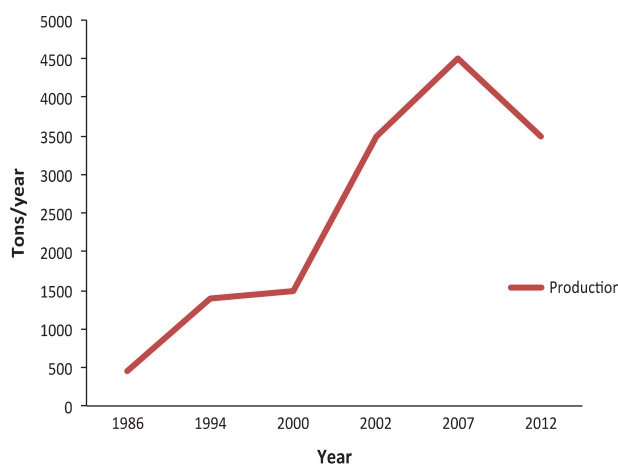


Fig. 1. World total Joboba oil production.

In addition, the use of Joboba meal after the extraction process is being thoroughly studied, especially its main component named Simmondsin, in order to increase the global interest of the Joboba cultivation. Simmondsin reduces the food intake because it induces a satiation process which can be avoided by its simultaneous use with a specific receptor antagonist [17]. The study conducted by Cokelaere et al. [17] proved that the anorexic effect of the Simmondsin is associated to mild pancreatic hypertrophy and stimulation of the interscapular brown adipose tissue. This fact was confirmed by Ham et al. [18] when they tried two different concentrations of Joboba meal and were added to the diet of Beagle dogs. When 2.7% of Joboba meal was part of the diet the dogs did not suffer reduction in their body weight and the food was completely digestible. However, the body weight and the digestibility of the food were affected at 8.1% dose [18]. As it was presented, 50% of the seed is transformed to Joboba meal after the extraction process [1] and therefore some applications should be taken into account in order to make the most of this waste. Joboba meal is rich in proteins (32%) and that is why it has been used as animal feed even though it is formed by 15% of toxic glycosides [19,20]. Many researchers have focused their attention on this waste in order to obtain high-added value products. For example, Abbassy et al. [21] isolated two glucosides from the seeds of Joboba plant (simmondsin and simmondsin-2'-ferrulate) which have insecticidal activity against *spodoptera littoralis*, antifungal activity against pathogenic fungi and antifeedant properties as it has been tested in other studies [22–24]. Moreover, it has been proved by Al-Anber et al. [25] that the use of defatted Joboba can succeed in the removal of methylene blue from aqueous water which is a harmful contaminant with an associated serious environmental impact. Another study was conducted by Harry-O'Kuru [26] and it consisted of the extraction of two simmondsin analogues DMS (Dimethylsimmondsin) and DDMS (Didemethylsimmondsin). These analogues have olefinic functional groups, easily converted to epoxides, which are intermediates with further potential uses such as plasticizers, aerosols, insecticides, epoxy resins or coatings. Finally, Joboba meal can be used as biomass because it has a high heating value (15.34 MJ/kg), and it also can be used in an anaerobic digestion for obtaining biogas from this waste (600 ml per 400 g of Joboba meal) [27,28].

2.1. Extraction process

Mechanical pressing of the Joboba seeds together with a hexane extraction of the pressed Joboba meal is the traditional way to obtain Joboba oil [10]. The combination of the mechanical pressing

Table 1
Jojoba seed and hulls composition.

Component (%w/w)	Whole seed	Dehulled whole seed	Hulls	Dehulled meal
Moisture	0.8	4.3	10.7	8.9
Proteins	15.1	14.9	7	29.1
Crude oil	50.2	53.8	0.7	3
Crude fiber	4.2	3.5	15.6	2.1
Ash	1.6	1.4	4.4	3.1
Total sugars	29.3	3.7	3.3	8.7

Refs. [29–31].

Table 2
Composition and properties of Jojoba oil.

Esters	Percent
<i>Composition</i>	
C34–C36	0.2
C38	6.6
C40	30.2
C42	50.9
C44	9
C46–C50	0.9
<i>Properties</i>	
Melting point (°C)	9
Density (g/ml)	0.862
Iodine value (g/100 g)	83
Acid value	0.36
Viscosity (cSt)	26.6
Moisture (%)	0.03
Flash point (°C)	225
CFPP (°C)	10
Oxidation stability (h)	41.3

Ref. [8].

with the organic solvent extraction is necessary because between 3% and 8% of the oil cannot be extracted only by mechanical process [1]. The composition of the whole seed, the dehulled whole seed, the hull and the dehulled meal is charted in Table 1. As shown in Table 1, the seed is formed mainly by crude oil and sugars and the main objective of the extraction process is to get as much

oil as possible, which is about a 50% of the whole seed. Table 2 reflects the composition in terms of the size in the chain of the monounsaturated esters and the most important properties of the extracted oil.

In addition, the extraction process also can only be conducted by the use of organic solvents such as hexane, but the main drawback is the amount of solvent and time that must be used in the process, which makes it inefficient from an economic perspective. Also, there are many environmental limitations regarding the use of dangerous solvents in the traditional extraction process and there have been many efforts in order to find cleaner methods in the production of Jojoba oil. One of these methods is the use of supercritical fluids, such as the CO₂, for the extraction of Jojoba oil because of the associated advantages of CO₂ as a solvent [10] such as it is inexpensive and completely inert. Nevertheless, the use of high pressures makes this process still unattractive, economically speaking. For that reason, different co-solvents could be used in order to increase the solubility of the CO₂ in the Jojoba oil [32] such as ethanol or propane. The main problem with the use of ethanol as co-solvent occurs after the depressurization process because it remains in the oil phase and; therefore, it could affect the properties of the final extracted product if it is not properly removed. In the case of propane, the main disadvantage is its flammability although this fact can be controlled at certain propane/CO₂/air mixture proportions [10].

The different methods of Jojoba oil extraction that researchers have tested are charted in Table 3. The maximum yield of

Table 3
Extraction methods of Jojoba oil.

Type of extraction				
Pressing process	Type of press	Number of pressing	Pretreatment process	% Oil
[2]	Hydraulic	1	None	35.4
	Hydraulic	2	Breaking	43.8
[33]	Rosedowns	1	Preheating	38.2
	Hander	1	Preheating	35–39
	Hander	2	Preheating	40–42
	Hander	3	Preheating	43
[34]	Hydraulic	1	Preheating, cracking, flaking	30.8
Extraction with solvents	Solvent	Time	Particle size (mm)	% Oil
[2]	Hexane	18	<1 mm	52
	Chloroform	18	<1 mm	32.5
	Isopropanol	18	<1 mm	45
	Toluene	18	<1 mm	44.8
[35]	Hexane	6	0.23	52.8
[36]	Hexane	–	0.48	55
[37]	Water	2	–	40
Supercritical Extraction	T (K)	P (bar)	Solvent	% Oil
[32]	343	450	scCO ₂	0.44 gO/g
[35]	363	600	scCO ₂	50.6
[10]	313	70	30%CO ₂ + propane	98 ^a

^a Extractable material.

extraction depends on the content of oil in the seed and in many cases this value is slightly higher than 50%. In addition, the yield reached by mechanical pressing could be increased by the use of organic solvents in order to guarantee that all the extractable compounds are removed from the seed.

2.2. Direct use and blending

One of the main reasons of the high price of this special kind of oil is the numerous applications that Jojoba oil have in the chemical industry and in fine chemicals. These applications depend on the physical and chemical properties of the oil. Thanks to these unique properties the oil has a well-known and defined structure which is related to a high grade of purity. In addition Jojoba oil presents high oxidation stability, it remains in liquid state at room temperature and it has a great potential to be subjected to polymerization and hydrogenation reactions [38].

The results of Habashy et al. [9] showed that Jojoba oil reduces carrageenin-induced paw oedema because of its antinflammatory activity. Jojoba oil was used by ancient natives in American continents for inflammatory diseases because it diminished the prostaglandin E₂(PGE₂) level in the inflammatory exudates. The production of 11-eicosenoic acid by hydrolysis of Jojoba oil using lipases turns in the release of free fatty acids which reduces the production of PGE₂ [9]. Also, Jojoba oil was used by Guirguis et al. [39] for improving the antimicrobial activity of chitosan against two different microorganisms *Staphylococcus Aureus* and *Bacillus Subtilis*. This way, the potential of chitosan can be enhanced for food safety and many biomedical applications [40].

In addition, Santo et al. [41] studied the application of Jojoba oil as an alternative collector for the selective separation of apatite and calcite minerals in an acid medium without the use of depressants. The optimum concentration of Jojoba oil for this study was reached at 200 mg/l. Another application of this oil was studied by Touitou and Godin [42] and consisted of the production of non-permeating sunscreens by the immobilization of UV-absorbing substances on Jojoba oil. This formula prevents adverse skin and systemic reactions related to transdermal absorption when conventional sunscreens are used.

Moreover, Braden et al. [43] studied the effect of different substances in the preoperative anxiety in surgical patients. The study was based on testing lavender and Jojoba oil in different groups of people in order to observe the possible reduction of the anxiety in the selected patients. This study concluded that the use of essential oils is a good mechanism to increase the overall health satisfaction of the patients who need surgery.

The company Colgate-Palmolive [44] has demonstrated that the quality of their body wash products is related to the moisturizer effect of the Jojoba butter present in their composition. Therefore this is one of the most important applications of Jojoba oil and it explains its high utilization in the cosmetic market nowadays.

Finally, Shehata and Abdel Razeq [45] made a comparison between conventional diesel with a blend formed by 20% Jojoba oil + 80% diesel in terms of quality as fuel and associated emissions using a diesel engine. It was concluded that the use of the Jojoba oil/diesel blend reduced the brake thermal efficiency, the brake power and the break effective pressure. On the other hand, the mentioned blend increases the brake specific fuel consumption. Regarding generated emissions, the use of Jojoba oil/diesel blend in the engine increases the production of CO and CO₂. Nevertheless the NO_x emissions are reduced when Jojoba oil/diesel blend is used instead of conventional diesel. Moreover, Al-Widyan and Al-Muhtaseb [27] used pure Jojoba oil and a mixture of 50% Jojoba oil + 50% diesel and they compared their performance regarding conventional diesel in a cylinder diesel engine. The results led to a similar conclusion as Shehata and Abdel Razeq [45] in terms of

reduction of NO_x when Jojoba oil or its mixture with conventional diesel. Nevertheless, taking into account the high price of Jojoba oil currently the use of more affordable oils or biodiesel from inexpensive raw materials for fuel purposes is much more sensible than such valuable oil with many more applications in the fine chemical industry or cosmetics market.

3. Esterification to obtain Jojoba oil analogues and direct transesterification

As said before, Jojoba oil and spermaceti are the main raw materials formed by monounsaturated esters. Since whales are endangered, their hunting is under strict control of the International Whaling Commission [46]. In addition, Jojoba growth is limited to some desert areas. These two facts have meant a raise in the price of these monounsaturated esters and their related alcohols and in the search of new alternatives to replace these valuable products [47]. Researchers have studied in the last two decades the esterification of oleic acid with different alcohols in order to substitute the lack of natural sources to obtain monounsaturated esters.

On the other hand, Jojoba oil can be used in many chemical transformations because of the presence of two double bonds and an ester group [1]. Among the reactions that this oil can be subjected to, researchers have studied isomerization, hydrogenation, halogenation, sulfuration, sulfur halogenation, oxidation, ozonolysis, epoxidation and many more transformations [1]. However, the transesterification of Jojoba oil using different catalysts have been thoroughly reported by many researchers because Jojoba oil is a non-edible oil and biodiesel from this raw material belongs to 2nd generation biofuels. The methanolysis of Jojoba oil is shown in Fig. 2 where fatty acid methyl esters together with monounsaturated alcohols are produced. Thus, alkyl esters derived from the Jojoba oil transesterification can be used as fuel after its separation from long chain monounsaturated alcohols making the overall process more profitable [8].

In this section, esterification processes to obtain Jojoba oil analogues and direct transesterification reactions that have been already reported are charted in Table 4 and will be itemized and evaluated.

3.1. Homogeneous alcoholysis reactions

Transesterification reaction can be carried out homogeneously, heterogeneously or using enzymes. However, the advantages associated to the use of homogeneous catalysts for producing biodiesel have converted this catalytic way the most used at industrial scales. Concretely, the base-catalyzed alcoholysis using sodium and potassium methoxides and hydroxides are the most established way to obtain biodiesel since these catalysts have a high activity, easy availability and are inexpensive [48,49]. In addition, the base-catalyzed alcoholysis conveys a fast process using moderate reaction conditions. Nevertheless, these catalysts should be used when the acidity of the oil is lower than 1% and the raw

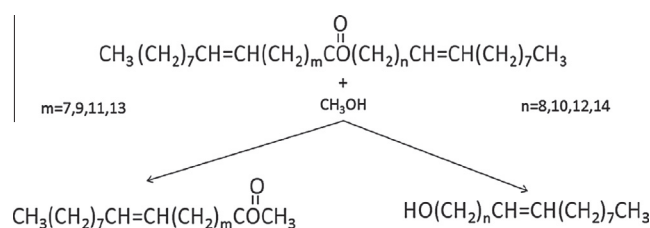


Fig. 2. Scheme of the transesterification of Jojoba oil.

Table 4

Catalysts for alcoholysis of Jojoba oil.

Reference	Catalyst	Alcohol	Catalyst	Alcohol:oil ratio	Temperature/time	Performance
[53]	CH ₃ OK	Methanol	1.5%	6:1	60 °C/5 h	94% (conversion)
[53]	CH ₃ OK	Ethanol	1.5%	6:1	75 °C/5 h	92% (conversion)
[53]	CH ₃ OK	1-Propanol	1.5%	6:1	78 °C/5 h	82% (conversion)
[53]	CH ₃ OK	1-Butanol	1.5%	6:1	85 °C/5 h	78% (conversion)
[54]	NaOH	Ethanol	1%	–	60 °C/1 h	93% (purity)
[55]	NaOH	Methanol	1%	–	60 °C/1 h	84.5% (yield)
[55]	KOH	Methanol	0.7%	–	60 °C/1 h	61.3% (yield)
[55]	Dibutyltin diacetate	Methanol	1%	23:1	60 °C/33 h	92.6% (yield)
[55]	Diocetyl tin diacetate	Methanol	1%	23:1	60 °C/33 h	25.4% (yield)
[55]	Dibutyltin oxide	Methanol	1.25%	23:1	60 °C/33 h	23.3% (yield)
[55]	Diocetyl tin oxide	Methanol	1.25%	23:1	60 °C/33 h	22 % (yield)
[55]	Diphenyltin oxide	Methanol	1.25%	23:1	60 °C/33 h	12% (yield)
[55]	MCD	Methanol	1%	23:1	60 °C/33 h	2.15 (yield)
[55]	MOH	Methanol	1%	23:1	60 °C/33 h	1.05% (yield)
[57]	CH ₃ ONa	Methanol	1%	7.5:1	60 °C/4 h	Approx. 90% yield
[58]	NaOH	Methanol	1%	–	65 °C/4 h	93% purity
[59]	KOH	Methanol	1.25%	6:1	30 °C/1 h	83.3% (yield)
[60]	KOH	Methanol	0.5%	6:1	60 °C/3 h	90.5% (yield)
[61]	CH ₃ CH ₂ ONa	Ethanol	–	Approx. 4:1	Microwave 90 W/3 min	Approx. 90% (conversion)
[62]	NaOH	Methanol	1%	–	60 °C/1 h	92% yield
[8]	CaO	Methanol	8%	9:1	65 °C/10 h	93.3% (conversion)
[76]	DBD organotin (IV) carboxylate	Methanol	0.01%	32:1	65 °C/48 h	89% (conversion)

MCD: Monobutyltin Chloride Dihydroxide.

MOH: Monobutyltin Hydroxide Oxide Hydrate.

materials used in the transesterification reaction are completely anhydrous in order to reduce the presence of secondary reactions such as neutralization and saponification [50]. Moreover, the reaction product after alcoholysis using homogeneous catalysts needs purification steps such as washing and vacuum distillation which make the process much less efficient. In addition, the initial impurities of the oil have a high impact on the final performance of base homogeneous catalysts [48]. This problem is solved with the use of acid homogeneous catalysts such as sulfuric or phosphoric acids in raw materials with high content in free fatty acids (FFA) because esterification and transesterification reactions can be conducted simultaneously. Nevertheless, acid homogeneous catalysts have a reduced activity regarding base catalysts, tedious purification steps are required and they become ineffective with a certain presence of water [50–52].

In the case of the transesterification of Jojoba oil using homogeneous catalysts the purification of the product after the reaction entails many more complications regarding the rest of the oils composed by triglycerides. As said before, the molecular structure of Jojoba oil is not formed by triglycerides but long monounsaturated esters [1]. Therefore, the product after alcoholysis of Jojoba oil does not have glycerol in their composition and the possibility of intermediate decantation steps is removed for this process [8]. Taking into account that decantation steps for eliminating glycerol, part of the homogeneous catalyst and other impurities are not possible in the Jojoba oil transesterification process, displacement of the reaction towards the formation of products takes much longer than conventional raw materials. After base-catalyzed alcoholysis of Jojoba oil the product is formed by monounsaturated alcohols together with alkyl esters, unreacted oil, a surplus of short-chain alcohol and the catalyst in only one phase. This fact implies the use of high amount of a strong washing agent (HCl) whereas the transesterification of conventional oils such as sunflower, rapeseed or palm oils requires a moderate washing agent such as distilled water or a citric acid solution in a volume five times less than Jojoba transesterified washing step [8]. Thus, the transesterification of Jojoba oil requires much longer time and the yield of the overall process is affected by the purification step which needs a strong agent and higher volume than purification of conventional oils.

Regarding homogeneous catalysis of Jojoba oil, El-Boulifi et al. [53] reported that the reactivity of short-chain alcohols in the alcoholysis of Jojoba oil using potassium methoxide as catalyst is reduced as the linear molecule becomes longer due to steric effects. The short-chain alcohols tested in this study were methanol, ethanol, 1-propanol and 1-butanol whereas the reaction conditions were 1.5% of catalyst content, 5 h of reaction time and different temperatures depending on the reactive used. The used temperatures were 60, 75, 78 and 85 °C for methanol, ethanol, 1-propanol and 1-butanol respectively in order to reach the equilibrium at a final time of 8 h. The oil conversion obtained in this study of the methanolysis, ethanolysis, propanolysis and butanolysis of Jojoba oil were 94, 92, 82 and 78% respectively.

Another study performed by Al-Awed et al. [54] studied the transesterification of Jojoba oil using ethanol and NaOH as catalyst and they also tested blends of the biodiesel obtained with ethanol in diesel engines. The optimum reaction conditions in the ethanolysis were temperature of 60 °C, 1% of catalyst percent and 1 h of reaction time. The purity of ethyl esters reached 93% under these reaction conditions.

Moreover, Shah et al. [55] studied different homogeneous and heterogeneous catalysts in the transesterification of Jojoba oil with methanol. The homogeneous catalysts that the study tested were NaOH, KOH, dibutyltin diacetate and dioctyltin diacetate at the following reaction conditions: 60 °C of reaction temperature, 23:1 methanol to oil ratio and a catalyst percent close to 1%. Among the catalysts studied the most active one was dibutyltin diacetate with an associate oil conversion of 92.6% after 33 h of reaction time. In another study conducted by Shah et al. [56] showed a maximum oil conversion (96%) after 2000 min with the use of dibutyltin diacetate as catalyst. In addition, Canoira et al. [57] studied the methanolysis of Jojoba oil using sodium methoxide as catalyst under the following reaction conditions: 1% of catalyst percent, 60 °C of reaction temperature, 7.5:1 methanol:oil ratio and 4 h of reaction time. The reached yield under the aforementioned conditions was close to 90%. A similar method as Canoira et al. [57] was conducted by Shailesh et al. [58] with the use of NaOH as catalyst. The conditions of this study were 65 °C of reaction temperature, 1% of catalyst percent and 4 h of reaction time where the purity of the product reached 93%.

Also, the methanolysis of Jojoba oil has been tested under low temperatures using KOH as catalyst by Bouaid et al. [59]. According to this study the maximum yield of esters can be obtained at 30 °C of reaction temperature, 1.25% of catalyst content, 6:1 methanol: oil ratio, 600 rpm of agitation speed and 1 h of reaction time. Under these reaction conditions the reached yield is 83.3% proving that the methanolysis of Jojoba oil can be carried out at ambient temperature with excellent results. Additionally, Fatah et al. [60] studied the methanolysis of Jojoba oil using KOH at higher temperatures and they observed that the maximum yield (90.5%) is reached after 3 h of reaction time, 6:1 methanol: oil ratio, at 60 °C of reaction temperature, 0.5% catalyst content and 1000 rpm stirrer velocity.

Thus, Hussein et al. [61] tried to reduce the reaction time of the transesterification of Jojoba oil using microwave technique and a homogeneous catalyst (sodium ethoxide). The reaction was conducted using ethanol, isopropanol, pentanol and octanol as short-chain alcohols. The extent of the reaction was around 90% depending on the short-chain alcohol after 3 min of reaction time at 90 W of microwave power.

Finally, Radwan et al. [62] studied the methanolysis of Jojoba oil using NaOH as catalyst, the use of seawater in the purification of the esters and the temperature of the washing agent. They concluded that the maximum yield (92%) is reached at 60 °C of reaction temperature, 1% of catalyst percent and 1 h of reaction time using seawater at 5 °C for the purification step.

3.2. Heterogeneous alcoholysis reactions

The interest in heterogeneous catalysts for conducting the transesterification reaction has augmented exponentially in the last decade because of the problems in the separation and purification steps derived from the use of homogeneous catalysts [49]. In addition, heterogeneous catalysts can be reused many times in the alcoholysis reaction improving the overall process economically and environmentally. There have been many reports related to the use of heterogeneous catalysts for the alcoholysis of vegetable oils [63] such as alkali metal oxides and derivatives [64,65], alkaline earth metal oxides and derivatives [66,67], transition metal oxides and derivatives [68], mixed metal oxides and derivatives [69], ion exchange resins type acid heterogeneous catalyst [70], sulfated oxides as an acid heterogeneous catalyst [71], carbon based heterogeneous catalysts [72] and waste material [73]. Nevertheless, there are few drawbacks related to the use of heterogeneous catalyst for the production of biodiesel compared to the homogeneous base catalysts such as slower reaction rate, mass transfer limitations, higher pressures and temperatures to reach competitive yields and the lack of practical knowledge at industrial scale. To date, the only industrial process for the biodiesel production based on the use of heterogeneous catalysts is the EsterFip which was developed by the French Institute of Petroleum [74].

When it comes to carrying out the Jojoba oil transesterification, the use of heterogeneous catalyst is even more interesting because it makes the overall process more feasible. As aforementioned, the purification and separation steps become more unaffordable because of the non-existence of triglycerides in the chemical structure of Jojoba oil. That is why, some studies have focused their attention on the use of heterogeneous catalysts for performing the alcoholysis of this special oil. For example, Sánchez et al. [8] optimized the Jojoba oil methanolysis using CaO derived from the calcination of mussel shells (*Mytilus Galloprovincialis*) by obtaining the kinetics of the reaction. The best conditions to perform the methanolysis of Jojoba oil using this renewable catalyst are 65 °C, 9:1 methanol:oil ratio, 8% of catalyst content and 10 h of reaction time where the oil conversion reached 93.3%. Sánchez

et al. [75] also studied the process at pressurized environment where the highest conversion of Jojoba oil (98%) was reached at 140 °C, methanol:Jojoba oil ratio of 6 and 6% of catalyst percent after 5 h of reaction time. The kinetic model obtained for the study conducted at atmospheric pressure and pressurized can be found in Eqs. (1) and (2) respectively, where both mechanism fit a sigmoidal curve because mass transfer limitations. In addition, Shah et al. [54] also studied the use of heterogeneous catalyst to conduct the Jojoba oil transesterification. The solid catalysts tested in this study were dibutyltin oxide, dioctyltin oxide, diphenyltin oxide, monobutyltin chloride dihydroxide and monobutyltin hydroxide oxide hydrate and the maximum yields reached were 22, 23.3, 12, 2.15 and 1.05% respectively under the following reaction conditions 60 °C of reaction temperature, 23:1 methanol to oil ratio and a catalyst percent close to 1%. Therefore, these heterogeneous catalysts are not active enough to conduct the methanolysis of Jojoba oil at higher scales.

$$\frac{dx_A}{dt} = \frac{7292.02 \cdot e^{(-13,158/RT)} \cdot 3.302 \cdot 10^{-7} \cdot g_{cat}^0 \cdot C_{M,0}^{0.89} \cdot T^0 (1 + 59.7 \cdot x_A^{0.23})}{7292.02 \cdot e^{(-13,158/RT)} + 3.302 \cdot 10^{-7} \cdot g_{cat}^0 \cdot C_{M,0}^{0.89} \cdot T^0 (1 + 59.7 \cdot x_A^{0.23})} \cdot (1 - x_A) \quad (1)$$

$$\frac{dx_A}{dt} = \frac{28.96 \cdot e^{(-3063/RT)} \cdot 3.5 \cdot 10^{-16} \cdot g_{cat}^{0.06} \cdot C_{M,0}^{2.13} \cdot T^{4.14} (1 - 0.92 \cdot x_A^{6.26})}{28.96 \cdot e^{(-3063/RT)} + 3.5 \cdot 10^{-16} \cdot g_{cat}^{0.06} \cdot C_{M,0}^{2.13} \cdot T^{4.14} (1 - 0.92 \cdot x_A^{6.26})} \cdot (1 - x_A) \quad (2)$$

Finally, Sirajuddin et al. [76] studied the methanolysis of Jojoba oil using organotin carboxylates as catalysts which have crystal structure and are soluble in organic solvents. These catalysts are usually prepared by condensation reactions of organotin oxides or hydroxides and carboxylic acids but there are many other ways to synthesize them [77]. The study concluded that DBD organotin (IV) carboxylate permits to reach 89% oil conversion under the following conditions: 65 °C, 0.01% of catalyst content, 48 h of reaction time and 32:1 MeOH to oil ratio. They also concluded that the use of higher amount of methanol could generate emulsions and difficulties in the purification step.

3.3. Enzymatic and heterogeneous esterification reactions

Many different researchers have focused their attention on obtaining Jojoba oil and spermaceti analogues from different raw materials in order to eliminate the problems associated to the lack of these natural resources. Therefore, the search of obtaining long monounsaturated esters from esterification reactions has been thoroughly investigated in the last few decades.

One of these studies was performed by Sánchez et al. [78] conducting the esterification reaction of oleic acid and oleyl alcohol using Y-zeolite as catalyst. The product of this reaction is oleyl oleate that is a Jojoba oil analogue and it has important applications as lubricant for high-speed machinery [79]. The reaction mechanism consists of the fast protonation of the oleic acid and the subsequent nucleophilic attack of the oleyl alcohol. The best reaction conditions to carry out the esterification are 180 °C of reaction temperature, 0.2% of catalyst content and 16 mmHg of pressure in order to reach a maximum yield of 45%. The same reaction was studied by Macedo and Lopes [80] using Lipozyme TL IM as catalyst where the maximum yield was 94.2% after 2 h of reaction time and using 9.8% of catalyst content and 1:3 acid:alcohol ratio. Moreover, Lopes et al. [81] concluded in a different study that the non-commercial lipase *Rhizopus* sp has a similar activity than the Lipozyme TL IM. However, García [82] studied the esterification

reaction using the same catalyst and the study concluded that 95.6% conversion is reached at 70 °C, after 2 h of reaction time, 1:1 acid:alcohol ratio and 5% of catalyst content. Moreover, Radzi et al. [83] also studied the esterification of oleic acid with oleyl alcohol but using Novozym 435 as catalyst. In this case, the yield was higher than 90% at 37 °C, after 3 h of reaction time and using an acid:alcohol ratio of 1:2. Finally, Isono et al. [84] studied the same esterification reaction using Lipase-surfactant complex as catalyst and this study led to 70% acid conversion after 24 h using an acid:alcohol ratio 1:1.

However, other kinds of alcohols can be used in the esterification of oleic acid for obtaining Jojoba oil analogues. For example, García [85] studied the esterification of oleic acid with cetlyl alcohol using Novozyme 435 as catalyst. At optimum conditions the acid conversion was 91.01% at 75 °C, 2 h of reaction time using 5% of catalyst content and an acid:alcohol ratio of 1:1. The same reaction was conducted by Li et al. [86] but using *Candida* sp 99–125 as catalyst and after 24 h of reaction time, at 40 °C, 10% of catalyst content and an acid:alcohol 1:0.9, the reached conversion was 95%. Finally, Rani et al. [87] performed the esterification of oleic acid with decanol using Novozyme 435 in order to obtain decyl oleate which can be used as lubricant and it has applications as moisturizer, sunscreen, eye shadows and eye creams. The study concluded that 96.53% of acid conversion is reached at 45 °C, after 1 h of reaction time, 1:1 acid: alcohol ratio and 2.5% of catalyst content.

4. Properties of transesterified Jojoba and its derivatives

Once the Jojoba oil transesterification process is finished the product obtained is formed by fatty acid alkyl esters and long chain monounsaturated alcohols, as shown in Fig. 2. These long chain monounsaturated alcohols are essentially a mixture of

11-eicosenol, 13-docosenol and 15-tetracosenol which have pharmaceutical applications against enveloped viruses such as AIDS, the flu and Hepatitis C [8,88]. Therefore, there have been many efforts devoted to the separation of the fatty acid alkyl esters from these valuable alcohols through different crystallizations steps [8,54,88–90]. For example, Aracil et al. [86] studied the crystallization of Jojoba transesterified with methanol by using different pure solvents and solvent mixtures and this report concluded that the highest yield of separation (98%) is reached when hexane:diethyl ether 3:1 mass ratio is used at –20 °C after two crystallizations steps. A summary of the results of this study is charted in Table 5.

The main properties of the products derived from the Jojoba oil transesterification and its subsequent crystallization are shown in Table 6. The products charted in Table 6 are, on one hand; Jojoba transesterified using different short-chain alcohols (methanol, ethanol, 1-propanol and 1-butanol) just after the alcoholysis process and, on the other hand; the jojobyl alcohols, fatty acid methyl esters (FAME), fatty acid ethyl esters (FAEE), fatty acid propyl esters (FAPE) and fatty acid butyl esters (FABE) which are the products obtained after the crystallization steps [52]. According to the results of Table 5, the Jojoba transesterified has a worse properties as fuel than its associated alkyl esters because of the presence of the jojobyl alcohols in the molecular structure. As shown in Table 6, viscosity, density, cold properties and oxidation stability are clearly improved in the fatty acid alkyl esters after crystallization steps regarding Jojoba transesterified. In the case of the jojobyl alcohols, the fulfillment of the UNE EN 14214 is not fundamental because the use of these alcohols are destined for pharmaceuticals and not as fuel.

Among the fatty acid alkyl esters presented in Table 6 the most interesting is the FABE because of its low cold properties and high oxidation stability although its viscosity is the highest regarding the rest of the fatty acid alkyl esters. Therefore, the cold properties

Table 5
Crystallization of long chain unsaturated alcohols after two steps at –20 °C.

Solvents	Ratio	Alcohols (g)	Yield (%)	%R20	%R22	%R24
Hexane/diethyl ether	1:1	36.2	88	42.2	48.2	9.1
Hexane/diethyl ether	2:1	39.6	91	43.2	46.9	9.3
Hexane/diethyl ether	3:1	48.9	98	37.3	52	9.9
Hexane		41.8	93	37.1	51	11
Hexane/ethyl acetate	3:1	27.8	84	30.9	56	13
Hexane/dichloromethane	3:1	28.6	81	43.8	44	12
Hexane/ethanol	3:1	31.2	83	39	48	13
Hexane/methanol	3:1	29.8	84	40	48	12
Pentane/diethyl ether	3:1	47.3	97	37.7	51.2	10.2
Pentane		43.1	96	37.4	51	11
Diethyl ether		35.7	86	36	50	14

Ref. [88]. R20: 11-eicosenol, R22: 13-docosenol, R24: 15-tetracosenol.

Table 6
Main properties of the products derived from the Jojoba oil transesterification and its subsequent crystallization.

	Density (kg/m ³)	Viscosity at 40 °C (mm ² /s)	FP (°C)	CV (MJ/kg)	CFPP (°C)	CP (°C)	PP (°C)	OS (h)	IV (I ₂ /100 g)	References
<i>Jojoba transesterified</i>										
Methanol	863–866	11.82–19.2	61–75	42.17–47.38	4.0–7.0	6	6	2.05	80	[4,53,54,57,88,90,91]
Ethanol	852–882	14.1	–	47.38	6	5	3.0–8.0	3.19	–	[53,54]
1-Propanol	891	16.8	–	–	3	4	0	4.38	–	[53]
1-Butanol	907	18.3	–	–	–1	1	–3	6.15	69.1	[53]
<i>After crystallization</i>										
FAME	836–871	7.5–10.4	–	42.82	–5	–2	–6	3.05	74.7	[53,57,88]
FAEE	853	8.24	–	–	–6	–3	–7	4.83	76.1	[53]
FAPE	861	9.03	–	–	–7	–6	–8	6.06	–	[53]
FABE	876	9.82	–	–	–8	–11	–12	6.89	63.8	[54]
Jojobyl alcohols	–	25.1	–	–	>25	–	–	3.1	78.8	[50,88]

FP: Flash Point CV: Calorific Value CFPP: Cold Filter Plugging Point CP: Cloud Point PP: Pour Point OS: Oxidation Stability IV: Iodine Value

are improved as the short-chain alcohol is augmented because of the reduction in the freezing point [53]. Regarding the oxidation stability, it is improved as the short-chain alcohols used in the alcoholysis are increased because of the augmentation of the molecular weight [53]. Nevertheless, the kinematic viscosity has the opposite tendency because this property tends to improve as the alcohol used in the transesterification is shorter [53]. In order to solve the problem associated to the high viscosity of the Jojoba methyl esters [89] studied the way to reduce this property through two different ways: increasing the temperature and adding diethyl ether to the methyl esters. This way, the ignition period delay is reduced, the maximum combustion pressure is increased and the maximum heat release is risen meaning a higher effectiveness in the diesel engine. Yet, not a single of the fatty acid alkyl esters charted in Table 5 can be used directly in a diesel engine because they do not fulfill the minimum requirements marked by the European legislation, however these FAEE can be mixed with other better-quality biodiesel from different raw materials [92] or burnt it directly in an electric generator [89,90].

Regarding emissions related to the combustion of Jojoba methyl esters, Saleh [93] conducted a study using a two-cylinder direct injection diesel engine and they concluded that the NO_x emissions can be reduced using the exhaust gas recirculation (EGR) technology. However, EGR also leads to a 17% increase in the brake specific fuel consumption which generates higher emissions of CO and HC [93,94] than in conventional diesel. Therefore, Attia and Hassaneen [95] conducted a study where alumina nanoparticles are added into Jojoba methyl esters in order to improve the combustion quality of the fuel so that reduce the emissions of NO_x and CO.

5. Future research opportunities

Currently, Jojoba oil is highly valuable in the market because of its many different applications in fine chemistry, pharmaceuticals

and cosmetics, as aforementioned. Moreover, biodiesel has experienced a huge increase in its production in the last decades because it reduces the consumption of conventional fossil fuels which have a negative impact on the environment. Therefore, the value of the Jojoba oil might be maximized by the implementation of a biorefinery because high-added value products such as mixture of long monounsaturated alcohols is produced as main product whereas a stream of fatty acid alkyl esters together with unreacted oil is obtained as co-product. This idea was conducted by Sánchez et al. [89] simulating a Jojoba oil biorefinery using a waste from fish industry as catalyst. In addition, economical assessment of the simulated biorefinery was carried out by the same authors [90]. The economic study concluded that the designed plant is completely profitable if the price of the jojobyl alcohols mixture raises to \$520/kg which is highly feasible taking into account that the price of the pure alcohols is higher than \$40/g. The catalyst used for the design of the plant was CaO derived from the calcination of mussel shells using the kinetic model obtained by the same authors in another study [8]. As explained before, the use of heterogeneous catalyst, such as CaO or MgO, for the transesterification of Jojoba oil is advantageous because of the problems linked to the washing and purification steps. This fact can be seen in the variance between the flow diagrams associated to the homogeneous process (Fig. 3) and the heterogeneous process (Fig. 4) where the purification of the Jojoba transesterified is conducted differently. In Fig. 3 can be seen that the Jojoba oil after homogeneous transesterification reaction needs to be washed, centrifuged and distilled before crystallization process. However, in Fig. 4 the heterogeneous process only entails a filtration of the catalyst and a flash distillation to prepare the Jojoba transesterified before the separation of the jojobyl alcohols from the fatty acid alkyl esters. As seen in Figs. 3 and 4, the biorefinery is divided in three steps which are: transesterification step, where the oil is transesterified and prepared for the separation process; crystallization step,

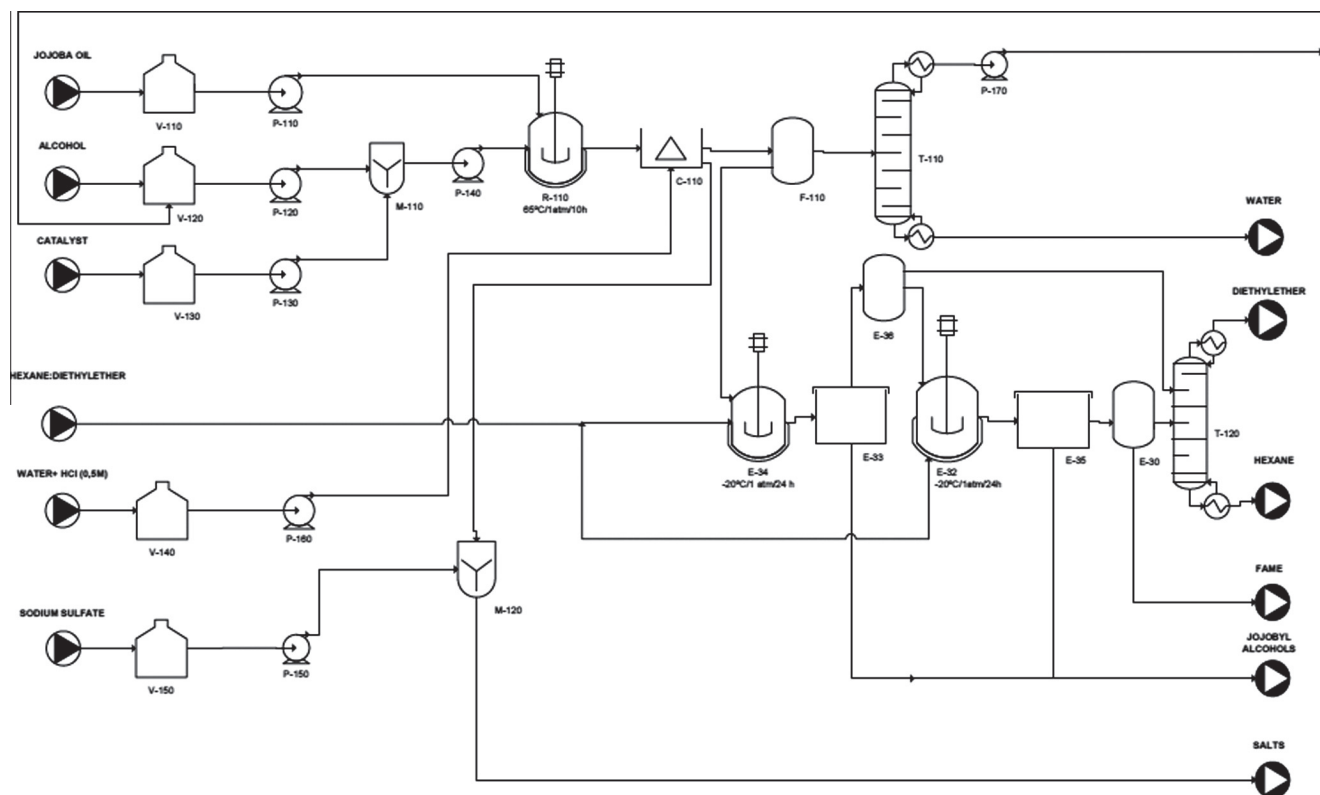


Fig. 3. Homogeneous transesterification process flow diagram [53].

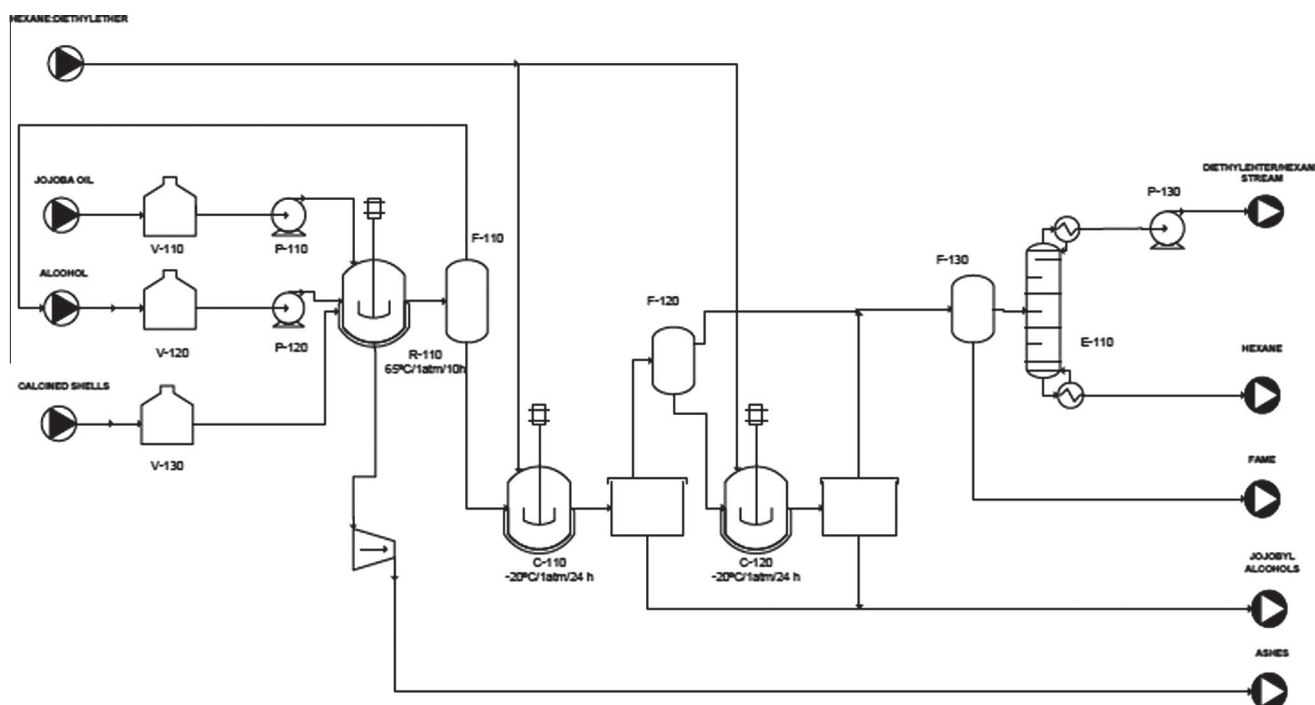


Fig. 4. Heterogeneous transesterification process flow diagram [89].

where the jobohyl alcohols are separated from the FAAE through a two-step process, and purification step, where the hexane and diethyl ether used in the crystallization are rectified to obtain hexane with a purity higher than 95% to increase the profitability of the overall process.

However, the biorefinery simulated by Sánchez et al. [89,90] has several recommendations to improve the feasibility of the process. First of all, the reaction time using CaO as catalyst in the methanolysis of Jojoba oil is about 10 h to reach 93.3% conversion and this time should be lowered by the use of a more active catalyst and/or pressure reactor. Secondly, there should be a search for an environmentally-friendly mixture of solvents to conduct the crystallization process because after this separation process hexane and diethyl ether need to be treated properly for reducing their impact on the environment. Thirdly, if this environmentally-friendly combination of solvents is not found another way to perform the separation of FFAE from jojobyl alcohols, such as high-vacuum distillation, might improve the profitability of the process. Finally, the final purpose of this biorefinery would be to obtain pure jojobyl alcohols (11-eicosenol, 13-docosenol, 15-tetracosenol) and not a mixture of them, therefore, the use of membrane filtration might allow to achieve this challenging goal. For example nanofiltration can be used for improving the separation of compounds with similar molecular weights and the enhancement in the high-added value products obtaining [96]. In addition, the organic solvent nanofiltration (OSN) is applied for the isolation of high-added value products [97] and it contributed to reduce the payback time of some process considerably [98].

Another way to make the most of Jojoba oil is the use of methods at high temperatures and pressures such as the non-catalytic cracking proposed by Kozliak et al. [99]. This study concludes that the maximum organic liquid product (OLP) yield is 93% and it is reached at 14.8 bar and 420 °C after 3 min of reaction time. The product of reaction is mainly formed by a mixture of a linear saturated short-chain fatty acids and alkanes. Thus, the study also performed the non-catalytic cracking to soybean oil and higher amount of undesirable viscous compounds are produced because of the triglyceride structure of the conventional oil. Therefore,

either catalytic or non-catalytic cracking can be conducted in jojoba oil in order to produce bio kerosene [100] since the use of fatty acid alkyl esters as jet fuel presents problems such as high freezing point or low calorific value and lower quality of the final product is obtained by using conventional oils [99,101].

Finally, since both extraction and alcoholysis of Jojoba oil entail their own complications, simultaneous extraction/transesterification might be the proper procedure to solve the drawbacks aforementioned. Several researchers have studied the in-situ transesterification of seeds because the cost of the process can be reduced up to 70% [102] and the use of co-solvents such as hexane can improve substantially the rate of the transesterification. For example, Barekati-Goudarzi et al. [103] used seeds of Chinese tallow trees to conduct the in-situ transesterification in a microwave-batch system using n-hexane as co-solvent where the optimal yield (89.19%) was reached at 58.1 °C, 1.74 wt.%, solvent ratio about 3 (v/w) after 20 min of reaction time. Moreover, jatropha seeds were also used by Kartika et al. [104] in a simultaneous process using n-hexane as cosolvent and KOH as catalyst and they obtained the highest biodiesel yield (87%) with 6:1 methanol to seed ratio, stirring speed of 800 rpm, a temperature of 50 °C, after 5 h of reaction time. Also, jatropha seeds were utilized in the study conducted by Lim et al. [105] in a simultaneous supercritical extraction/transesterification using different cosolvents such as pentane, heptane, toluene, tetrahydrofuran, nitrogen and carbon dioxide. Among these co-solvents, pentane and CO₂ proved their higher performance (FAME yield about 100%) under the following conditions: temperature of 280 °C, 4.0 ml/g methanol to solid ratio after 30 min of reaction time. Therefore, the use of a simultaneous extraction/transesterification technology in the case of the Jojoba seeds might mean a significantly improvement in the production of long chain monounsaturated alcohols from an economical and environmental points of view.

6. Conclusions

In the last decades, Jojoba plant has captured great interest among researchers and companies because of their unique charac-

teristics and physico-chemical properties, especially when spermaceti market was banned by the International Whaling Commission in 1986. The production of Jojoba has almost been multiplied by 10 in twenty years and the demand of oil visibly exceeds its production. Taking into account this information, it is expected that the cultivation of Jojoba plant will grow exponentially together with the search of synthetic ways to obtain similar waxy products in the next few years to fulfill the lack of natural resources which provide long monounsaturated esters. In addition, researchers have shown a growing concern in the possible uses of Jojoba meal, such as removal of contaminants or insecticides, in order to take advantage of the waste generated after extraction. The applications of Jojoba oil are numerous in pharmaceuticals or cosmetics and it can be used in many different reactions such as hydrogenation, halogenation or sulfuration to obtain high-added value products. However, the research of Jojoba oil has been mainly focused on the alcoholysis of this oil and NO_x , CO and CO_2 emissions related to the use of different blends of Jojoba oil and conventional fuel in a diesel engine. Recently, there have been also studies related to the separation of the products generated after Jojoba oil transesterification reaction and therefore the obtaining of long chain monounsaturated alcohols separated from fatty acid alkyl esters. From these studies, it is concluded that the mixture of long monounsaturated alcohols (11-eicosanol, 13-docosenol and 15-tetracosanol) produced after crystallization has a high value in the market because of its pharmaceutical properties against enveloped viruses whereas the co-product might be used for energy purposes. This could be the starting point for a biorefinery implementation undertaking the following points:

- Use of Jojoba meal for producing bioenergy or useful products.
- Improvement of the reaction step by the use of more active catalysts or procedures.
- Enhancement of crystallization step by the application of green solvents or change in the separation method.
- Research related to the separation of the jojobyl alcohols mixture to produce pure long monounsaturated alcohols.

Therefore, Jojoba has a promising future because it offers a bunch of opportunities in chemical and environmental sectors although several drawbacks linked to its cultivation, oil extraction and products purification after transesterification should be dealt with before its general exploitation.

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References

- [1] Wisniak Jaime. Potential uses of Jojoba oil and meal – a review. *Ind Crops Prod* 1994;3:43–68.
- [2] Abu-Arabi MK, Allawzi MA, Al-Zoubi HS, Tamimi A. Extraction of Jojoba oil by pressing and leaching. *Chem Eng J* 2000;76:61–5.
- [3] Yang L, Takase M, Zhang M, Zhao T, Wu X. Potential non-edible oil feedstock for biodiesel production in Africa: a survey. *Renew Sustain Energy Rev* 2014;38:461–77.
- [4] Ashraf AM, Masjuki HH, Kalam MA, Rizwanul Fattah IM, Imtihan S, Shahir SA, Mobarak HM. Production and comparison of fuel properties, engine performance, and emission characteristics of biodiesel from various non-edible vegetable oils: a review. *Energy Convers Manage* 2014;80:202–28.
- [5] Farghaly FA, Galal HK, Radi AAF, Abdel-Basset R. Nitrate-drought interactions on growth, osmoprotectants and antioxidant system of the oil accumulating desert plant Jojoba. *J Biol Earth Sci* 2013;3(1):30–41.
- [6] Al-Widyan MI, Al-Muhtaseb MA. Experimental investigation of Jojoba as a renewable energy source. *Energy Convers Manage* 2010;51:1702–7.
- [7] Ranzato E, Martinotti S, Burlando B. Wound healing properties of Jojoba liquid wax: an in vitro study. *J Ethnopharmacol* 2011;134:443–9.
- [8] Sánchez M, Marchetti JM, El Bouilfi N, Aracil J, Martínez M. Kinetics of Jojoba oil methanolysis using a waste from fish industry as catalyst. *Chem Eng J* 2015;262:640–7.
- [9] Habashy RR, Abdel-Naim AB, Khalifa AE, Al-Azizi MM. Anti-inflammatory effects of Jojoba liquid wax in experimental models. *Pharmacol Res* 2005;51:95–105.
- [10] Palla C, Hegel P, Pereda S, Bottin S. Extraction of Jojoba oil with liquid CO_2 + propane solvent mixtures. *J Supercrit Fluids* 2014;91:37–45.
- [11] ICIS chemical business; 2004. <http://www.icis.com/resources/news/2004/10/08/618904/rosy-future-expected-for-jojoba-producers-as-global-demand-continues-to-strengthen/>.
- [12] Annual world production of Jojoba; 2000. <http://www.prota4u.org/protav8.asp?en=1&p=Simmondsia+chinensis>.
- [13] Carlsson AS. Production of wax esters in crambe. CPL Press Science Publishers; 2006. ISBN 10: 1-872691-03-X.
- [14] After 15 year scientific research on Simmondsia Chinensis; 2007. http://users.telenet.be/jojoba/simmondsine/doc/state_of_the_art.pdf.
- [15] Seifert RW, Leleux BF, Tucci CL. Nurturing science-based ventures: an international case perspective. Springer; 2008. ISBN 978-1-846-28873-9.
- [16] El Bassam N. Handbook of bioenergy crops: a complete reference to species, development and applications. Routledge; 2010 [ISBN-13: 978-1844078547].
- [17] Cokelaere M, Daenens P, Decuyper E, Flo G, Kuhn E, Van Boven M, Vermaut S. Reproductive performance of rats treated with defatted Jojoba meal or simmondsin before or during gestation. *Food Chem Toxicol* 1998;36:13–9.
- [18] Ham R, Vermaut S, Flo G, Cokelaere M, Decuyper E digestive performance of dogs fed a Jojoba meal supplemented diet. *Ind Crops Prod* 2000;12:159–63.
- [19] Elliger CA, Waiss AC, Lundin RE. Simmondsin, an unusual 2 cyanomethylenecyclohexyl glucoside from Simmondsia californica. *J Chem Soc Perkin Trans* 1973;1:2209–12.
- [20] Bellirou A, Bouali A, Bouammalib B, Boukhatem N, Elmtili BN, Hamala A, El-Mourabit M. Extraction of simmondsin and oil in one step from Jojoba seeds. *Ind Crops Prod* 2005;21:229–33.
- [21] Abbassy MA, Abdelgaleil SAM, Belal AH, Rasoul MAA. Insecticidal, antifungal and antifungal activities of two glucosides isolated from the seeds of Simmondsia chinensis. *Ind Crops Prod* 2007;26:345–50.
- [22] Abdelgaleil SAM, El-Aswad AF. Antifeedant and growth inhibitory effects of tetranortriterpenoids isolated from three meliaceous species on the cotton leafworm *Spodoptera littoralis* (Boisd.). *J Appl Sci* 2005;1:234–41.
- [23] Abdel-Mageed WM, Bayoumi SALH, Salama AAR, Salem-Bekhit AM, Abd-Alrahman SH, Sayed HM. Antioxidant lipoxigenase inhibitors from the leaf extracts of Simmondsia chinensis. *Asian Pac J Trop Med* 2014;7(1):S521–6.
- [24] Gonzalez-Coloma A, Reina M, Diaz CE, Fraga BM. Natural product-based biopesticides for insect control. *Compr Nat Prod II* 2010;3:237–68.
- [25] Al-Anber ZA, Al-Anber MA, Al-Ayed MMO, Omari NM. Defatted Jojoba for the removal of methylene blue from aqueous solution: thermodynamic and kinetic studies. *Desalination* 2011;276:169–74.
- [26] Harry-O'kuru RE. Modification of simmondsin and its demethylated analogues. *Ind Crops Prod* 2000;12:215–21.
- [27] Al-Widyan MI, Mu'taz Al-Muhtaseb. Experimental investigation of Jojoba as a renewable energy source. *Energy Convers Manage* 2010;51:1702–7.
- [28] Al-Hamamre Z, Rawajfeh KM. Investigating the energy value of Jojoba as an alternative renewable energy source. *Int J Green Energy* 2016;12:398–404.
- [29] Cottagorge AG, Weber CW, Reid BL, Price RL. Detoxification of Jojoba seed meal. In: Proceedings of the third international conference on Jojoba and its uses, Riverside, Calif., p. 171–84.
- [30] Watanabe T, Takanashi K, Matsuda K. Carbohydrates of Jojoba seed: isolation and characterization of xyloglucan. In: Proceedings of the third international conference on Jojoba and its uses, Riverside, Calif., p. 83–105.
- [31] Verbiscar AJ, Banigan TF. Composition of Jojoba seeds and foliage. *J Agric Food Chem* 1978;26:1456–9.
- [32] Salgin U. Extraction of Jojoba seed oil using supercritical CO_2 + ethanol mixture in green and high-tech separation process. *J Supercrit Fluids* 2007;39:330–7.
- [33] Rawles LR. In: Proceedings of the third international conference on Jojoba and its uses. Riverside, CA: University of California; 1978. p. 279–83.
- [34] Spadaro JJ, Lambou MG. In: Proceedings of the first international conference on Jojoba and its uses, Tucson, Ariz., Office of Arid Lands Studies College of Earth Sciences, University of Arizona; 1972. p. 47–60.
- [35] Salgin U, Çamili A, Zühtü Uysal B. Supercritical fluid extraction of Jojoba oil. *J Am Oil Chem Soc* 2004;81:293–6.
- [36] Allawzi MA, Abu-Arabi MK, Al-Taher FA. Parametric study on the batch leaching process of jojoba oil. *Eur J Lipid Sci Technol* 2005;107:469–75.
- [37] Bellirou A, Bouali A, Bouammalib B, Boukhatem N, Elmtili BN, Hamal A, El-Mourabit M. Extraction of simmondsin and oil in one step from Jojoba seeds. *Ind Crops Prod* 2005;21:229–33.
- [38] Sánchez M. Monounsaturated long-chain alcohols production from Jojoba oil using a green catalyst. PhD Thesis; 2015.
- [39] Guirguis OW, Abd Elkader MFH, Nasrat AA. Enhancing antimicrobial activity for chitosan by adding Jojoba liquid wax. *Mater Lett* 2013;93:353–5.
- [40] Dutta PK, Tripathi S, Mehrotra GK. Perspectives for chitosan based antimicrobial films in food applications. *Food Chem* 2009;114:1173–82.
- [41] Santos EP, Dutra AJB, Oliveira JF. The effect of Jojoba oil on the surface properties of calcite and apatite aiming at their selective flotation. *Int J Miner Process* 2015;143:34–8.

- [42] Touitou E, Godin B. Skin nonpenetrating sunscreens for cosmetic and pharmaceutical formulations. *Clin Dermatol* 2008;26(4):375–9.
- [43] Braden R, Reichow S, Halm MA. The use of the essential oil lavandin to reduce preoperative anxiety in surgical patients. *Am Soc Perianesth Nurs* 2009;348–53.
- [44] Colgate-Palmolive introduces new Palmolive body wash variants in India focus on surfactants, vol. 8; 2012, p. 4.
- [45] Shehata MS, Abdel Razek SM. Experimental investigation of diesel engine performance and emission characteristics using Jojoba/diesel blend and sunflower oil. *Fuel* 2011;90:886–97.
- [46] Overview about whales; 2016. <http://www.worldwildlife.org/species/whale>.
- [47] Franssen MCR, Steunenberg P, Scott EL, Zuillhofa H, Sanders JPM. Immobilised enzymes in biorenewables production. *Chem Soc Rev* 2013;42:6491–533.
- [48] Avhad MR, Marchetti JM. A review on recent advancement in catalytic materials for biodiesel production. *Renew Sustain Energy Rev* 2015;50:696–718.
- [49] Sánchez M, Aracil J, Martínez M. Current status and prospects of biodiesel production from brassica species. *Int Rev Chem Eng (IRECHE)* 2013;5:342–50.
- [50] Tariq M, Ali S, Khalid N. Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: a review. *Renew Sustain Energy Rev* 2012;16:6303–16.
- [51] Baskar G, Aiswarya R. Trends in catalytic production of biodiesel from various feedstocks. *Renew Sustain Energy Rev* 2016;57:496–504.
- [52] Issariyakul T, Dalai AK. Biodiesel from vegetable oils. *Renew Sustain Energy Rev* 2014;31:446–71.
- [53] El-Boulifi N, Sánchez M, Martínez M, Aracil J. Fatty acid alkyl esters and monounsaturated alcohols production from Jojoba oil using short-chain alcohols for biorefinery concepts. *Ind Crops Prod* 2015;69:244–50.
- [54] Al Awad AS, Selim MYE, Zeibak AF, Moussa R. Jojoba ethyl ester production and properties of ethanol blends. *Fuel* 2014;124:73–5.
- [55] Shah M, Ali S, Tariq M, Khalid N, Ahmad F, Khan MA. Catalytic conversion of Jojoba oil into biodiesel by organotin catalysts, spectroscopic and chromatographic characterization. *Fuel* 2014;118:392–7.
- [56] Shah M, Tariq M, Ali S, Guo Q, Fu Y. Transesterification of Jojoba oil, sunflower oil, neem oil, rocket seed oil and linseed oil by tin catalysts. *Biomass Bioenergy* 2014;70:225–9.
- [57] Canoira L, Alcántara R, García-Martínez MJ, Carrasco J. Biodiesel from Jojoba oil-wax: transesterification with methanol and properties as a fuel. *Biomass Bioenergy* 2006;30:76–81.
- [58] Shah Shailesh N, Sharma Brajendra K, Moser Bryan R, Erhan Sevim Z. Preparation and evaluation of Jojoba oil methyl esters as biodiesel and as a blend component in ultra-low sulfur diesel fuel. *Bioenergy Res* 2010;3:214–23.
- [59] Bouaid A, Bajo L, Martinez M, Aracil J. Optimization of biodiesel production from Jojoba oil. *Process Saf Environ Prot* 2007;85:378–82.
- [60] Fatah MA, Farag HA, Ossman ME. Production of biodiesel from non-edible oil and effect of blending with diesel on fuel properties. *IRACST – Eng Sci Technol: Int J (ESTIJ)* 2012;2:583–91.
- [61] Hussein LI, Elsabee MZ, Ismail EA, Naguib HF, Aziz HA, Elsaywy MA. Transesterification of Jojoba oil-wax using microwave technique. *World Acad Sci Eng Technol Int J Environ, Chem, Ecol, Geol Geophys Eng* 2014;8:287–91.
- [62] Radwan MS, Ismail MA, Elfeky SMS, Abu-Elyazed OSM. Jojoba methyl ester as a diesel fuel substitute: preparation and characterization. *Appl Therm Eng* 2007;27:314–322.59.
- [63] Puna JF, Gomes JF, Bordado JC, Correia MJN, Dias APS. Biodiesel production over lithium modified lime catalysts: activity and deactivation. *Appl Catal A* 2014;470:451–7.
- [64] Evangelista JP, Gondim AD, Souza L, Araujo AS. Alumina-supported potassium compounds as heterogeneous catalysts for biodiesel production: a review. *Renew Sustain Energy Rev* 2016;59:887–94.
- [65] Lu H, Yu X, Yang S, Yang H, Tu S. MgO–Li₂O catalysts templated by a PDMS–PEO comb-like copolymer for transesterification of vegetable oil to biodiesel. *Fuel* 2016;165:215–23.
- [66] Roschat W, Siritanon T, Yoosuk B, Promarak V. Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. *Energy Convers Manage* 2016;108:459–67.
- [67] Istadi I, Prasetyo SA, Nugroho TS. Characterization of K₂O/CaO–ZnO catalyst for transesterification of soybean oil to biodiesel. *Procedia Environ Sci* 2015;23:394–9.
- [68] Kwong T, Yung K. One-step production of biodiesel through simultaneous esterification and transesterification from highly acidic unrefined feedstock over efficient and recyclable ZnO nanostar catalyst. *Renew Energy* 2016;90 (450–45):7.
- [69] Gurunathan B, Ravi A. Biodiesel production from waste cooking oil using copper doped zinc oxide nanocomposite as heterogeneous catalyst. *Bioresour Technol* 2015;188:124–7.
- [70] Jaya N, Selvan B, Karpanai, Vennison S John. Synthesis of biodiesel from pongamia oil using heterogeneous ion-exchange resin catalyst. *Ecotoxicol Environ Saf* 2015;121:3–9.
- [71] Shi G, Yu F, Wang Y, Pan D, Wang H, Li R. A novel one-pot synthesis of tetragonal sulfated zirconia catalyst with high activity for biodiesel production from the transesterification of soybean oil. *Renew Energy* 2016;92:22–9.
- [72] Dhawane SH, Kumar T, Halder G. Biodiesel synthesis from Hevea brasiliensis oil employing carbon supported heterogeneous catalyst: optimization by Taguchi method. *Renew Energy* 2016;89:506–14.
- [73] Tan YH, Abdullah MO, Nolasco-Hipolito C, Taufiq-Yap YH. Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: catalyst characterization and biodiesel yield performance. *Appl Energy* 2015;160:58–70.
- [74] Bournay L, Casanave D, Delfort B, Hillion G, Chodorge J. New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catal Today* 2005;106:190–2.
- [75] Sánchez M, Avhad MR, Marchetti JM, Martínez M, Aracil J. Enhancement of the jojobyl alcohols and biodiesel production using a renewable catalyst in a pressurized reactor. *Energy Convers Manage* 2016;126:1047–53.
- [76] Sirajuddin M, Tariq M, Ali S. Organotin(IV) carboxylates as an effective catalyst for the conversion of corn oil into biodiesel. *J Organomet Chem* 2015;779:30–8.
- [77] Matela G, Aman R. Organotin (IV) complexes of carboxylic acid derivatives. *Centr Eur J Chem* 2012;10:1–15.
- [78] Sánchez N, Martinez M, Aracil J, Corma A. Synthesis of Oleyl Oleate as a Jojoba oil analog. *JAACS* 1992;69(11):1150–3.
- [79] Cirujano FG, Corma A, Llabrés i Xamena FX. Zirconium-containing metal organic frameworks as solid acid catalysts for the esterification of free fatty acids: synthesis of biodiesel and other compounds of interest. *Catal Today* 2015;257:213–20.
- [80] Macedo GA, Lopes DB. Optimization study of enzymatic synthesis of oleyl oleate, an analog of Jojoba oil, by response surface methodology. *New Biotechnol* 2009;25:152.
- [81] Lopes DB, Duarte MCT, Macedo GA. Biosynthesis of oleyl oleate wax ester by non-commercial lipase. *Food Sci Biotechnol* 2011;20(5):1203–9.
- [82] García T, Coterón A, Martínez M, Aracil J. Kinetic model for the esterification of oleic acid and cetyl alcohol using an immobilized lipase as catalyst. *Chem Eng Sci* 2000;55(8):1411–23.
- [83] Radzi SM, Basri M, Salleh AB, Ariff A, Mohammad R, Rahman MBA, Rahman RNZRA. High performance enzymatic synthesis of oleyl oleate using immobilized lipase from *Candida antarctica*. *Electron J Biotechnol* 2005;8:291–8.
- [84] Isono Y, Nakayama M, Nabetami H. Solvent-free esterification of oleic acid and oleyl alcohol using membrane reactor and lipase-surfactant complex. *J Ferment Bioeng* 1998;86:138–40.
- [85] García T, Martínez M, Aracil J. Enzymatic synthesis of an analogue of Jojoba oil: optimization by statistical analysis. *Enzym Microbial Technol* 1993;15 (7):607–11.
- [86] Li D, Xiaoqing W, Kaili N, Fang W, Junfeng L, Pu W, Tianwei T. Synthesis of Wax Esters by lipase-catalyzed esterification with immobilized lipase from *Candida sp.* 99–125. *Chin J Chem Eng* 2011;19(6):978–82.
- [87] Rani KNP, Neeharika TSVR, Kumar TP, Satyavathi B, Sailu C, Prasad RBN. Kinetics of enzymatic esterification of oleic acid and decanol for wax ester and evaluation of its physico-chemical properties. *J Taiwan Inst Chem Eng* 2015;55:12–6.
- [88] Aracil J, Martínez M, El-Boulifi N, Sánchez M, Serrano M. Proceso integrado de obtención de alcoholes monoinsaturados, biodiesel y productos biodegradables a partir de aceite de Jojoba. Spanish patent ES2494620; 2013.
- [89] Sánchez M, Marchetti J, El-Boulifi N, Aracil J, Martínez M. Jojoba oil biorefinery using a green catalyst. Part I: Simulation of the process. *Biofuels, Bioprod Biorefin* 2015;9(2):129–38.
- [90] Sánchez M, Marchetti J, El-Boulifi N, Aracil J, Martínez M. Jojoba oil biorefinery using a green catalyst. Part II: Feasibility study and economical assessment. *Biofuels, Bioprod Biorefin* 2015;9(2):139–46.
- [91] Selim MYE. Reducing the viscosity of Jojoba methyl ester diesel fuel and effects on diesel engine performance and roughness. *Energy Convers Manage* 2009;50:1781–8.
- [92] Serrano M, Oliveros R, Sánchez M, Moraschini A, Martínez M, Aracil J. Influence of blending vegetable oil methyl esters on biodiesel fuel properties: oxidative stability and cold flow properties. *Energy* 2014;65: 09–115.
- [93] Saleh HE. Experimental study on diesel engine nitrogen oxide reduction running with Jojoba methyl ester by exhaust gas recirculation. *Fuel* 2009;88:1357–64.
- [94] An H, Yang WN, Li J, Zhou DZ. Modeling analysis of urea direct injection on the NO_x emission reduction of biodiesel fueled diesel engines. *Energy Convers Manage* 2015;101:442–9.
- [95] Attia AMA, Hassaneen AE. Influence of diesel fuel blended with biodiesel produced from waste cooking oil on diesel engine performance. *Fuel* 2016;167:316–28.
- [96] Morthensen ST, Luo J, Meyer AN, Jørgensen H, Pinelo M. High performance separation of xylose and glucose by enzyme assisted nanofiltration. *J Membr Sci* 2015;492:107–15.
- [97] Marchetti P, Solomon MFJ, Szekely G, Livingston AG. Molecular separation with organic solvent nanofiltration: a critical review. *Chem Rev* 2014;114:10735–806.
- [98] Cao X, Wu XY, Wu T, Jin K, Hur BK. Concentration of 6-aminopenicillanic acid from penicillin bioconversion solution and its mother liquor by nanofiltration membrane. *Biotechnol Bioprocess Eng* 2001;6:200–4.
- [99] Kozlak E, Mota R, Rodríguez D, Overby P, Kubátová A, Stahl D, Niria V, Ogdenc G, Seames W. Non-catalytic cracking of Jojoba oil to produce fuel and chemical by-products. *Ind Crops Prod* 2013;43:386–92.
- [100] Hew KL, Tamidi AM, Yusup S, Lee KT, Ahmad MM. Catalytic cracking of bio-oil to organic liquid product (OLP). *Bioresour Technol* 2010;101:8855–8.

- [101] Cremonez PA, Feroldi M, Viana de Araújo A, Borges MN, Meier TW, Feiden A, Teleken JG. Biofuels in Brazilian aviation: current scenario and prospects. *Renew Sustain Energy Rev* 2015;43:1063–72.
- [102] Velasquez-Orta SB, Lee JGM, Harvey AP. Evaluation of FAME production from wet marine and freshwater microalgae by in situ transesterification. *Biochem Eng J* 2013;76:83–9.
- [103] Barekati-Goudarzi M, Boldor D, Nde DB. In-situ transesterification of seeds of invasive Chinese tallow trees (*Triadica sebifera* L.) in a microwave batch system (GREEN3) using hexane as co-solvent: biodiesel production and process optimization. *Bioresour Technol* 2016;201:97–104.
- [104] Kartika IA, Yani M, Ariono D, Evon Ph, Rigal L. Biodiesel production from jatropha seeds: solvent extraction and in situ transesterification in a single step. *Fuel* 2013;106:111–7.
- [105] Lim S, Lee K. Influences of different co-solvents in simultaneous supercritical extraction and transesterification of *Jatropha curcas* L. seeds for the production of biodiesel. *Chem Eng J* 2013;221:436–45.