

Review:**Thermal Process of Castor and Plant Based Oil****Mohammad Haniff Ahmad¹, Wan Asma Ibrahim², Jahirah Sazali¹, Izirwan Izhab¹, and Zulkafli Hassan^{1,*}**¹Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia²Forest Research Institute Malaysia (FRIM), 52109 Kepong, Selangor Darul Ehsan, Malaysia*** Corresponding author:**

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Abstract: Castor oil is an oil derived from castor seed from the plant *Ricinus communis*. The versatility of castor oil is highly attributed by the 12-hydroxy-9-octadecenoic acid (ricinoleic acid) and its functional groups. It is an oil that cannot be consumed by humans. However, castor oil actually can be used to produce many valuable products such as chemicals, paint, and cosmetics due to its unique characteristic which contains a high percentage of ricinoleic acid that helps in producing many valuable products. The utilization of vegetable oils is currently in the highlight of the chemical industry, as they are one of the most important renewable resources due to their universal availability, inherent biodegradability, low price, and eco-friendliness. Therefore, the main aim of this paper is to focus on the thermal cracking of castor oil with Zeolite ZSM-5 as the catalyst generates products consisting alcohol, methyl esters and fatty acids which are valuable raw materials for industries. The background, characteristics, composition, properties and industrial application of castor oil have also been discussed. The important properties and various applications of castor oil which can be obtained from toxic seeds have much greater potential than other available vegetable oils.

Keywords: castor oil; ricinoleic acid; composition; industrial application

■ INTRODUCTION

Nowadays, Asia can be considered as the leader for oils and fats in the oleochemical industry. Specifically, 75% of the total production of castor oil was conquered by India and then followed by China and Brazil each accounting for 12.5 and 5.5%, respectively as shown in Fig. 1 [1]. This has made India the world's largest producer of castor oil. The world castor oil production has increased from 2003 to 2013 with the values from 1.055 to 1.440 million tons while India is leading it [4]. In a decade, the production has increased about 36% due to castor oil's easy availability, low cost, non-food competition, high boiling point, high viscosity and other environmental considerations [1]. As previously mentioned, Fig. 1 shows that Asia is truly leading the production of castor oil with India alone contributing most of it. To support more of this statement, castor oil Derivatives Market Global

Market Analysis Opportunity Outlook 2021 reported that Asia-Pacific dominates the global castor oil and derivatives market due to increasing healthcare spending and continuous expansion of personal care. Countries such as India and China are expected to further dominate the global market of castor oil and derivatives and flourish at a compound annual growth rate (CAGR) of 5.0% during 2015–2021 [2].

Castor plant grows well in wet tropics to the dry subtropical regions with an optimum temperature of 20–25 °C. Warm climate condition can attribute to the high content of oil, but temperatures over 35 °C can cause poor seed setting while lower temperatures can induce the formation of frost which can destroy the plant [3]. The poor climate adaptability of the plant to cold weather conditions has restricted the pursue of castor plantation. Besides that, high toxicity of the castor seed is also the reason why U.S. farmers do not pursue

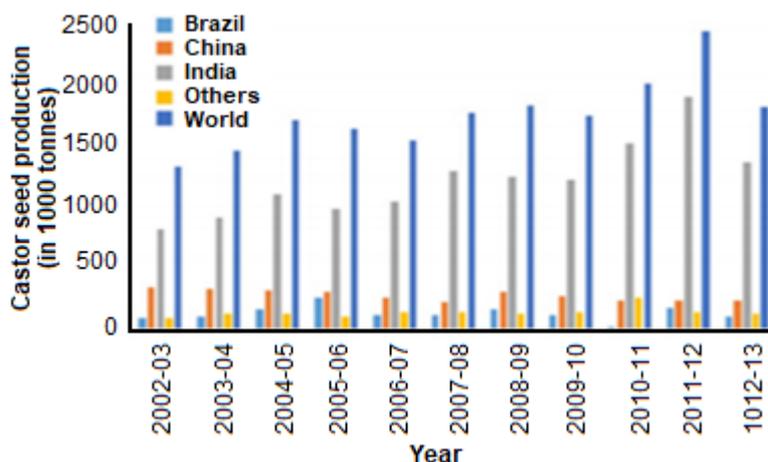


Fig 1. Production amount of castor oil by major countries. Reprinted (adapted) from Mubofu [1] with permission from Springer International Publishing



Fig 2. Castor plant, *Ricinus communis* (on the left) and Castor seeds (on the right)

castor plantation due to ricin that presents in the seed, where 1 mg of it can actually kill an adult [4]. Castor plant is mostly found in India where it grows wild on wastelands and is also cultivated for its oily seeds. Although castor plant is native to the Ethiopian region of tropical east Africa, it is becoming an increasingly abundant weed in the southwestern United States and also in tropical and warm temperate regions throughout the world [5]. Around 6000 years ago in Egypt, castor plant had already been grown for its oil [6].

In terms of physical appearance, castor plant can be grown as a large shrub or tree up to 12 m in height depending on the suitability of the climate. The stems of castor plant are hollow and pale green while the leaves are glossy reddish brown with obvious veins and are 10–40 cm

in length. The seeds are capsulated in a reddish green spiny fruit and dispersed by water and wind [2]. It takes around 95–180 days for the fruits to be ripe. The castor seed crop can be harvested when all the capsules are dry, and the leaves have fallen from the plants [7]. It is a crop that has potential in hot climates, and the yield is greatly affected by the soil moisture, photoperiod, and temperature of the production area [8].

Castor oil, *Ricinus communis* L., is originally a member of the tropical plant family Euphorbiaceae. Castor plant is usually planted and cultivated mostly in the temperate countries of the globe. Castor oil is a viscous, pale yellow, non-volatile and non-drying oil with a bland taste [4]. Castor oil is a non-drying oil with no odor, and it has high viscosity. It is yellowish brown

in nature as shown in Fig. 2. This oil comes from the castor seed of a plant called *R. communis* or generally called castor plant. The oil was obtained from the seed through a process of extracting or expressing it. Moreover, the castor seeds usually consist of 50% castor oil which can simply be extracted from its seeds. The versatility of castor oil has been applied in various sectors such as specialty chemicals, perfume, and medicine [9]. The interest for castor oil products in the market value is increasing which might be caused by their sustainability, biodegradability, eco-friendliness and their reasonable price [9].

The flexibility of castor oil is focused on its high composition of ricinoleic acid as well as the existence of the three functional groups. The carboxyl group can enlarge the esterification limit in which the unsaturation can be adjusted by hydrogenation, epoxidation or vulcanization process. The hydroxyl group plays an important role for the oil in producing a semi-drying state by making it acetylated or alkoxyated. Furthermore, the reactivity of the hydroxyl position allows the molecule to split through the extreme temperature of pyrolysis. Caustic fusion process helps to shorten the carbon chain to obtain products. The double bond, on the other hand, contributes to the ability for chemical reactions and it allows the modification process to happen. The hydroxyl group contributes to the high viscosity of castor oil [10]. Castor oil has an unsaturated bond, high molecular weight (298), low melting point (5 °C) and a very low solidification point (-12 to -18 °C). Thus, these characteristics make it industrially marketable, as it has the most stable viscosity among the other vegetable oils which brings a lot of advantages to castor oil [11]. Therefore, the suitable thermal process such as thermal catalytic cracking is crucial in order to obtain castor oil since the unique structure of castor oil contributes to the various industrial applications of castor oil.

■ EXTRACTION, COMPOSITION, AND PROPERTIES OF CASTOR OIL

The oil from castor seed can be extracted either by mechanical pressing and solvent extraction or a combination of both [12]. Firstly, the seed was crushed into small pieces and then dried in a steam-jacketed vessel so that the moisture content in the castor seed can be removed. Then, the crushed seed was inserted into hydraulic presses and pressed hard in order to extract the oil [4]. However, the oil recovered was not much, only around 45%, but there were still around 10% of the oil that can be extracted from the cake [12-13]. Therefore, further steps were taken to further extract the oil inside the cake by using a solvent extraction method. Through this method, most of the studies done by other researchers used Soxhlet extractor to extract the remaining oil inside the cake [4,14-15]. There is also a study which has been done by Mgudu et al. [16] where they performed a solvent extraction method assisted by microwave as the heating medium. Most of the solvent used from other studies for the solvent extraction method was hexane, but another solvent can also be used like heptane and petroleum ethers which then will help to remove the remaining oil inside the cake [3]. Table 1 shows the yield of castor oil obtained from several studies through the extraction process by a solvent extraction method using hexane as the solvent for the process. It was reported that cold-pressed oil has low acid value, low iodine value and a slightly higher saponification value than solvent-extracted oil and is lighter in color. However, there was still no information on which oil from these methods was used for the industries [4].

Castor seed usually contains about 30–35% of oil [17] but there are also studies stating that castor seed contains between 45–55 % of oil, but it depends on the

Table 1. The yield of castor oil through a solvent extraction process

Parameter	Warra [18]	Abdelaziz et al. [19]	Nangbes et al. [17]	Abitogun et al. [15]
Weight of seed (g)	50	910	-	-
Oil yield (%)	42.23 ± 0.208	31.99	48.32 ± 1.85	48.39 ± 2.00
Method	Solvent extraction	Solvent extraction	Solvent extraction	Solvent extraction

Table 2. Properties of castor oil

Properties	Yusuf et al. [21]	Salimon et al. [15]	Abitogun et al. [15]
Specific gravity	0.959	-	0.948
Lipid content (%)	-	43.30	-
Moisture content (%)	-	0.20	0.30
Iodine value (mg/g)	84.18	84.50	58.39
Acid value (mg/g)	2.07	4.90	14.80
% free fatty acid	-	3.40	7.40
Peroxide value (mq/kg)	38.00	10.20	158.64
Saponification value (mg/g)	175.31	182.90	178.00
Viscosity (cP)	-	332.00	-
Refractive index at 25°C	1.472 (30°C)	1.47	1.792
Average molecular weight	-	937.70	-
Fire point (°C)	-	-	256.00
Flash point (°C)	-	-	225.00
Smoke point (°C)	-	-	215.00
pH	6.16	-	5.80
Congealing temperature (°C)	-	-	18.00

Table 3. Compositions of fatty acids from various studies

Type of fatty acid	Ogunniyi [4] (%)	Mutlu [6] (%)	Salimon et al. [15] (%)	Abitogun [15] (%)
Ricinoleic	89.0	87.7 – 90.4	84.2	81.94
Palmitic	1.0	0.8 – 1.1	1.3	0.46
Oleic	3.0	2.2 – 3.3	5.5	2.28
Linoleic	4.2	4.1 – 4.7	7.3	0.61
Linolenic	0.3	0.5 – 0.7	0.5	0.30
Stearic	1.0	0.7 – 1.0	1.2	0.50
Dihydrostearic	0.7	-	-	0.24

method of extraction used and the geographical area [1]. Hence, various compositions and physical-chemical properties of castor oil were observed from castor seed in different climatic conditions [20]. For example, castor oil from Malaysia has a total lipids value of 43.3% per dry weight and saponification value of 182.96 mg KOH/g [12] whereas Nigerian castor oil contains total lipid value of 48% per dry weight and saponification value of 178.00 mg KOH/g [1].

In terms of properties, castor oil may have various physical and chemical properties as they depend greatly on the selected method of extraction. Table 2 shows the typical properties obtained from several other studies based on the solvent extraction method. The chemical composition of castor oil remains relatively constant

although it was grown in a different country of origin or season.

Similar to the other plant-based oils, castor oil is also a triglyceride molecule that mostly consists of fatty acids and glycerol [18,22]. What makes the castor oil special and comparatively unique is generally due to its plentiful composition of ricinoleic acid and also the presence of functional groups of hydroxyl and carboxyl with the single point of unsaturation existing in the molecule. Ninety percent of the fatty acids are accounted by the ricinoleic acid and marginal percentages of saturated and unsaturated components. Table 3 shows the composition of fatty acids that exist in castor oil from various studies analyzed through Gas Chromatography-Mass Spectrometry (GC-MS). The presence of ricinoleic

acid is the main factor why the castor oil is more valuable due to the various possible applications in the chemical industry.

The presence of ester linkage, hydroxyl and carboxyl groups of the castor oil aids to the versatility of oil through various chemical reactions and modification by undergoing certain processes with an added reactant to produce many valuable products. Fig. 3 shows the chemical structure of castor oil while Table 4 shows various reactions that castor oil can undergo with their final products from the respective processes.

■ INDUSTRIAL APPLICATION

For industrial purposes, castor oil is the most suitable alternative compared to other plant-based oils because it can be used as a starting or raw material for various industrial high-value-added products, typically due to its impressive chemical structure. Fig. 4 shows the structure of ricinoleic acid in castor oil with the presence

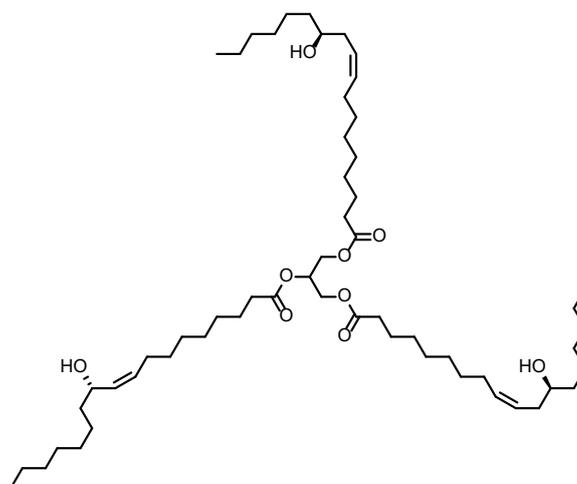


Fig 3. Structure of castor oil

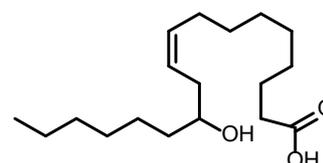


Fig 4. Chemical structure of ricinoleic acid

Table 4. Products from different reactions of castor oil [23]

Functional groups	Type of reaction	Added reactants	Type of products
Ester linkage	Hydrolysis	Acid, enzyme or Twitchell reagent catalyst	Fatty acids, glycerol
	Esterification	Monohydric alcohols	Esters
	Alcoholysis	Glycerol, glycols, pentaerythritol	Mono- and diglycerides monoglycols, etc.
	Saponification	Alkalies, alkalies plus metallic salts	Soluble soaps, insoluble soaps
Double bond	Amidation	Alkylamines, alkanolamines, and other compounds	Amine salts, amides
	Oxidation, polymerization	Heat, oxygen, crosslinking agent	Polymerized oils
	Hydrogenation	Hydrogen (moderate pressure)	Hydroxystearates
	Epoxidation	Hydrogen peroxide	Epoxidized oils
	Halogenation	Cl ₂ , Br ₂ , I ₂	Halogenated oils
	Addition reactions	S, maleic acid	Polymerized oils
	Sulphonation	H ₂ SO ₄	Sulphonated oils
	Hydroxyl group	Dehydration, hydrolysis, distillation	Catalyst (e.g., concentrated sulphuric acid, activated earth) (plus heat)
Caustic fusion		NaOH	Sebacic acid, capryl alcohol
Pyrolysis		High heat	Undecelynic acid, heptaldehyde
Halogenation		PCl ₅ , POCl ₃	Halogenated castor oils
Alkoxylation		Ethylene and/or propylene oxide	Alkoxyated castor oils
Esterification		Acetic-, phosphoric-, maleic-, phthalic anhydrides	Alkyl and alkylaryl esters, phosphate esters
Urethane reactions		Isocyanates	Urethane polymers
Sulfation		H ₂ SO ₄	Sulfated castor oil

of double bond and functional groups of hydroxyl and carboxyl. The high percentage of ricinoleic acid and the existence of the functional groups are the factors why castor oil has more possibilities and versatile applications in the chemical industry compared to the other vegetable oils [6]. Castor oil is usually used in the market as a raw material for various products like paint, lubricant, perfumes and other wide variety of products.

One of the applications of castor oil is in the manufacture of artificial leather. In this process, 50% of castor oil is mixed with 25% nitrocellulose and 25% cellulose and dispersed in a low-boiling solvent to be later applied to cloth [10]. This process has been fully developed until it is hard to differentiate whether the product is artificial or genuine leather. It is because the introduction of castor oil into nitrocellulose helps to yield a good quality of film concerning its strength and pliability [24]. Furthermore, the hydroxyl group also helps to endow it with a higher degree of miscibility with nitrocellulose than other fatty oils [24].

Castor oil was also used in the production of perfume because this oil can produce valuable chemicals such as heptaldehyde and undecylenic acid. The castor oil needs to undergo the transesterification process to obtain the methyl esters by previously mixing it with methanol before proceeding the process. The product will then be distilled and separated to obtain only methyl ester. Hence, the methyl ester will undergo thermal cracking process at a higher temperature around 500 °C to obtain the final product [25].

Lastly, castor oil is also possible to be utilized in paint manufacturing. Usually, paint contains vegetable oil such as linseed and tung oil where its function is to form tough films by covering the coated surface when it is exposed to atmospheric oxygen. This process is known as drying because both of these oils function as drying oils, mainly because they are highly unsaturated compared to castor oil that only has one double bond resulting in the lack of drying properties. According to Gilbert [24], the hydroxyl group of castor was possible to be removed as water which would cause the formation of second olefinic linkage to produce dehydrated castor oil (DCO) product which contains two double bonds in the fatty acid chain.

This dehydrated castor oil will dry paints films faster compared to linseed oil but less rapidly than tung oil [24].

■ THERMAL DEGRADATION

Biomass fuels from vegetable oils can be synthesized by utilizing various types of methods available. The most common methods used are pyrolysis, catalytic cracking [26], transesterification processes with the assistance of catalysts [27] and also hydrocracking reactions [28]. The products from the mentioned methods have high potential to be obtained from the vegetable oil [29]. The products of the thermal process usually consist of petroleum-like fractions such as gasoline, kerosene, diesel and no sulfur or heavy metals present [30].

On top of that, the biofuels produced by the catalytic cracking process are possible to be achieved by using the current infrastructure used in the oil refining industry. This is because the lab-scale catalytic cracking concept is very similar to the oil refining process. Therefore, biofuels have a promising industrial technology to be used and a high market demand.

Castor oil which undergoes thermal cracking process can yield mostly heptaldehyde and undecylenic acid. This happens when the ricinoleic molecule located at the hydroxyl is cleaved to be shorter chain molecules, in which the process is conducted at a high temperature without the presence of oxygen [31]. Both compounds have their applications in the market especially in cosmetics, pharmaceuticals, polymers, and perfumery. Heptaldehyde is also applicable as a solvent for resins and rubber production. According to Ogunniyi et al. [4], heptaldehyde can be used as a plasticizer by going through a hydrogenation process. Heptaldehyde is usually formed from the hydroformylation process of hexane, the esters of undecylenic and ricinoleic acid which has been degraded or through the hydrolysis of methyl undecenoate.

On the other hand, undecylenic acid is normally important in the preparation of insecticides, nylon from polymers and foot remedies. The other main applications of castor oil are paints or coatings. Castor

oil can produce special paint or furniture oil applications by going through dehydration by nonconjugated oil-maleic anhydride [6]. A study by Trevino and Trumbo [31] proved that the castor oil could be utilized for coating production by changing the hydroxyl of castor oil to β -ketoesters using *t*-butyl acetoacetate. This reaction is found to be comparatively fast and can be proceeded to high yield under delicate conditions. This is because the results showed that the 60° angle glosses of the films and film flexibilities were sensible. Castor oil is also most commonly used as biodegradable polyesters. Carothers has prepared the first synthetic condensation polymers in the 1930s [32]. Polyesters are highly biodegradable and environmentally friendly, with wide applications in the biomedical field, preparation of elastomers and packaging materials.

■ ZEOLITE ZSM-5 CRACKING

Zeolite catalyst ZSM-5 is one of the most efficient catalysts used for hydrocarbon cracking. It is made up of silica-alumina pentagon chains connected by oxygen atoms [33]. HZSM-5 is known for its ability to react with any materials to obtain aromatic and gasoline products. This catalyst will further assist the vegetable oils to obtain up to gasoline boiling range compounds. Other than that, the selectivity of zeolites fully depends on the acidity, pore shape, and size [34]. The usage of acidic zeolite catalyst such as ZSM-5 in catalytic cracking processes can be a promising choice to acquire olefins. In addition, the crystalline catalyst will provide a large surface area. This allows the cracking process to be initiated by the presence of active acid sites [35]. The selective characteristics of HZSM-5 based on shape will cause minor cracking which eventually produces a high amount of organic liquid products (OLP) and low amount of gaseous products [36].

Furthermore, catalysts with oxides such as calcium oxide will cause the delay in the decomposition of long-

chain oxygenated hydrocarbons. Therefore, the reactions using basic catalysts will obtain similar products as thermal cracking. However, secondary cracking is needed to form aromatic compounds.

The product to be obtained might differ greatly due to the presence of a catalyst. Zeolites are mostly used in major sectors such as petrochemical and pollution control. Furthermore, the high acidity contributes to the high efficiency in selectivity as well as the activity of zeolites, as compared to other amorphous silica-alumina catalysts. Zeolites are better as it is more powerful in cracking ability [37]. Few past works have been done using zeolites in order to crack vegetable oils [38]. Therefore, heterogeneous catalysis has the advantage by depending on the properties of the zeolites' materials used [33,35]. Different types of zeolites have also shown the impressive ability in catalytic cracking of different plant-based oils, such as HZSM-5 with supported metals [38]. Cracking, aromatization, isomerization of hydrocarbons, and alkylation reactions can easily happen when zeolite ZSM-5 is used. Some metals are commonly used to enhance zeolites effectiveness because of their ability to withstand the zeolites' acidity. Zeolite ZSM-5 has high silica over aluminum ratio. For instance, the catalytic cracking of camelina oil to yield biofuels using a different concentration of zinc incorporated into ZSM catalyst shows that higher concentration of zinc added did not give higher yield. The suitable zinc concentration must be less, around 20 wt.% in which this resulted in higher yield [39]. Besides, the incorporation of zinc into ZSM-5 can expedite decarbonylation and dehydrogenation processes [40-41]. However, the catalyst used might also become a constraint to the catalytic cracking process. Therefore, it is always encouraging to discard impurities as well as minimizing the viscosity of the oils used.

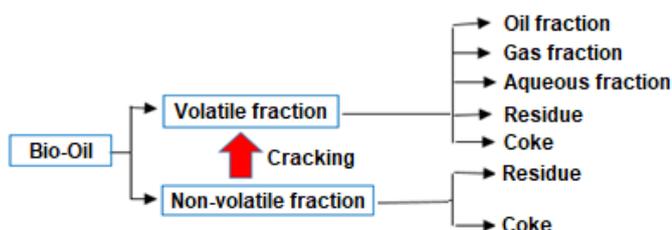
The thermal cracking process is used to observe the conversion of light olefins when it is being tested using

Table 5. Products obtained by using different types of ZSM-5 catalyst.

Catalyst type	Types of oil	Metal	Product	Reference
ZnZSM-5	Camelina	Zn	Acids, alcohols, esters, hydrocarbons	[39]
NaZSM-5	Crude soybean	Na	Aromatics, cyclics, aliphatics, acids, ketones	[43]
HZSM-5	Jatropha	-	Aliphatics, aromatics, esters, acids, ketones	[36]

Table 6. Type of catalysts used to yield oil products

Type of catalyst	Reaction temperature(°C)	The yield of oil (wt.%)	Reference
H-mordenite	330	17	[44]
ZnZSM-5	380	19	[45]
HZSM-5	380	24	[45]

**Fig 5.** Reaction chain

four kinds of HZSM-5 catalysts [42]. It is highly favorable to use the hydrogenation reactions to determine the profile of the process and for the deoxygenation of triglycerides to obtain hydrocarbons in a liquid state. Table 5 shows the typical products obtained from several other studies by using different types of ZSM-5 catalysts from three different types of vegetable oils.

■ ZEOLITES AS CATALYST FOR CRACKING REACTIONS

Generally, thermal cracking occurs at the ranges of temperature from 400 to 600 °C. Higher temperature tends to make lower oil product and higher gas product. This is because a higher temperature will increase the rate of reactions and thus, smaller volatile compounds can be formed. Oxygen content can also be decreased to an acceptable amount depending on the temperature needed. Zeolite cracking mechanism can be done through a few reactions. Firstly, hydrocarbons are cracked to smaller fractions. Next, oxygen is eliminated by dehydration as the main path through decarboxylation, and decarbonylation processes [40].

Further reaction mechanism of the zeolite cracking can be simplified into a reaction chain as shown in Fig. 5. Initially, bio-oil will be divided into a volatile and a non-volatile fraction conducted at 200 °C in vacuum condition [44]. The non-volatile fraction which underwent cracking can become volatiles, or it can become condensate through a polymerization process. It can also become the residue as it does not evaporate in the process. The volatile

fraction can consist of oil, liquid, and gaseous fractions. The volatiles can polymerize or condense in order to become residue as well. Table 6 shows the type of catalysts used to yield oil products.

■ CONCLUSION

In conclusion, castor oil is proved to be an important renewable source. Although it was not edible to be consumed by human, like other vegetable oils, there are so many uses that castor oil can be utilized in other industries to produce more valuable end products. The impressive composition of ricinoleic acid and the availability of the three functional groups of hydroxyl, carboxylate and double bond makes it as a highly potential renewable resource when it undergoes various chemical reactions, modifications, and transformations to produce derivative products. The thermal cracking approach is recognized as an efficient method to produce different kinds of specialty chemicals. In addition, thermal cracking is absolutely a reliable alternative for various sectors especially in the processing of specialty chemicals. Other than that, zeolite ZSM-5 has also displayed great potential as cracking catalysts. It is suggested to let the activity of cracking catalyst to be further improved by combining microporous zeolites with mesoporous materials in order to increase its thermal and hydrothermal stability and also its selectivity towards organic liquid products (OLP).

In this short review, it is outlined the background, characteristics, composition and various industrial uses of castor oil in the industries. However, there are still other chemicals or side products derived from the castor oil that can be produced which did not manage to be mentioned in this paper. For future directions, the non-edible oils like castor oil or other non-edible oils in the market should be further discovered through researches so that those edible oils in the market can be focused on as a source of food for human only. In order to secure

the availability of castor oil, fertile agricultural land should be allocated for edible oil plantation whereas waste or fallow land should be used for non-edible oil crops as it has simpler and easier ecological requirements. Limited land areas, especially in developed countries, should be fully utilized for non-edible oil plantation such as castor oil in which it will eventually increase the oil production for the country's economic assurance [46].

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