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Biodiesel production from corn oil: A review

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ABSTRACT

This paper deals with biodiesel production from corn oil as a feedstock via the transesterification and esterification reactions. To date, corn oil has not been considered a viable biodiesel feedstock because of its high edible value and relatively high price, but some industrial corn processing co-products, such as corn germ and dried distillers grains with solubles (DDGS), have potential for this application after the extraction of corn distillers oil (CDO). Here, after brief discussion of the issues related to corn botany, cultivation, and use, as well as the corn germ and oil composition, properties and use, the methods of corn processing for germ and DDGS recovery are presented. In addition, the mechanical and solvent extraction techniques for oil recovery from whole ground corn kernels, germs, and DDGS are considered. Furthermore, biodiesel production from corn oil, waste frying corn oil, and CDO is critically analyzed. It is expected that further investigation will be directed toward developing simpler, more effective and energy-saving technologies for biodiesel production from cornoil-based feedstocks, especially from CDO. The integration of biodiesel production directly into corn-based ethanol production will advance the overall economy of industrial plants. Furthermore, the fuel properties, performances and exhaust gas emissions of corn-based biodiesel and its blends with diesel fuel are discussed, taking into account the biodiesel quality standards. Finally, issues related to the environmental and socio-economic impacts of corn-based biodiesel production and use are also tackled.

1. Introduction

Biorenewable energy resources have attracted attention of governments, businesses and scientists globally because of rapid technological developments, obvious economic benefits and increased global warming and environmental pollution [1]. Among them, biodiesel is a very prospective alternative to mineral diesel fuel. Biodiesel is defined as a mixture of long chain fatty acid alkyl esters that meet the specified standards. Biodiesel is commonly produced by the esterification of free fatty acids (FFAs) or the transesterification (alcoholysis) of triacylglycerols (TAGs) from different biological renewable recourses, with an excess of methanol or ethanol, in the presence of an acid, base or enzyme catalyst, although non-catalytic processes are also possible. Global biodiesel production is expected to continue to expand in the upcoming years, rising from 29.7·10⁶ m³ in 2014–39·10⁶ m³ in 2024, a 27% increase [2]. This expansion is supported by the expectation that the global biodiesel price will remain almost unchanged until 2024 because of the projected decrease in vegetable oil prices. High production prices, caused by the high contribution (70–95%) of currently used oily feedstocks to the total production costs, is considered to be the primary barrier to the commercial use of biodiesel [3]. Therefore, other oil crops should be examined, especially those that could grow on marginal lands and produce non-edible oils. With the goal of biodiesel price reduction in mind, oil-containing co-products and waste from the existing production processes are also preferred as biodiesel feedstocks. Such co-products include corn germ (the portion of corn kernel that contains oil) from starch production and distillers dry grains with solubles (DDGS) from ethanol production [4,5].

Corn or maize (*Zea mays* L.) is an interesting oil crop that is produced in large quantities globally. In 2014, 1,060,107,470 and 3,189,137 t of corn crop and corn oil, respectively, were produced globally [6]. Large amounts of corn are used in starch and ethanol production, and corn oil is a by-product. The proposed ethanol production could generate $1.5.10^6$ m³ of corn distillers oil (CDO, i.e., whole

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stillage-extracted corn oil) from 56.8.10⁶ m³ of corn if the extraction degree is only 8.9 kg of oil per metric ton of corn [7]. Historically, corn oil has not been viable biodiesel feedstock because of its high value as an edible oil and relatively high price. However, there is a trend in the United States of America for the increasing use of CDO for biodiesel synthesis, representing the fastest expanding oily feedstock for biodiesel production in 2013 [8]. About 479,000 t CDO was used to produce biodiesel in 2015, compared with 51,000 t in 2010 [9]. Approximately 85% of dry grind ethanol plants in the United States of America extracted corn oil in 2015, producing about 1.22 10⁶ t CDO [10]. This offers the possibility for the integrated production of ethanol and biodiesel. Another positive effect of corn oil extraction is the reduction of induced land use emissions because of the integrated ethanol/biodiesel production, which is based on the same or smaller land area [11]. Aside from innovative technologies, a realistic way of increasing the quantity of corn oil is the use of corn varieties that produce a higher oil content compared to the currently grown varieties. The negative side of cornbased biodiesel might be the impact on food prices because greater demand for corn is expected to increase the prices of other crops competing for the same land. However, corn-based ethanol expansion of 3.8·10⁶ m³ (one billion gallons) increased the corn price by 3–4% in 2015, with even smaller projected changes in the future [12].

This paper provides a general overview of the usage of corn oil as oily feedstock for biodiesel production. First, corn cultivation, corn germ composition, and use, as well as corn oil composition, properties and use are briefly described. Then, the corn processing methods to recover corn germs and DDGS are presented. Furthermore, the techniques of oil recovery from whole ground corn kernels, corn germs, and corn DDGS are reviewed. Subsequently, biodiesel production from corn oil, waste frying con oil (WFCO) and CDO by catalytic and non-catalytic transesterification reactions is critically considered. Afterward, fuel properties, performances and exhaust gas emissions of corn-based biodiesel and its blends with diesel fuel are discussed, taking into account biodiesel quality standards. Finally, issues related to the environmental impact of corn-based biodiesel production and usage are tackled.

2. Botany, cultivation, and uses of corn

Corn (*Z. mays* L.) is an annual plant of an average height of 2.5 m with yellow or white grainy fruit. It belongs to the genus *Zea*, the family Poaceae (grasses), and the order Cyperales. The genus *Zea* consists of four species of which *Z. mays* L. is economically important and has a number of hybrids that differ from one another with respect to the chemical composition and grain structure [13]. The other *Zea* species (teosintes) are wild grasses native to Central America and Mexico.

Corn is widely cultivated all over the world, and each year its production increases more than that of any other grain product [14]. Today, corn is mostly grown in the United States of America (about 40%) and China (about 20%); other top producers are Brazil, Argentina, Indonesia, Ukraine, India, Mexico, Indonesia, and France [15]. Corn is mainly used as animal feed, as a raw material in industry, and, to a lesser extent, as human food (especially in the developing countries). Because of growing world population and the increased need for food, it is predicted that the production of corn will have surpassed the production of wheat and rice by 2050 [16,17]. The volume of corn production in the world is mostly attributed to the development of technology and seed industry, increased agro-efficiency, innovative corn food, and technical corn products, and, principally, innovation and increased production of bioethanol and biodiesel [18]. In Serbia, corn is considered the most suitable crop for alternative fuels production because of its large oversupply [19].

As human food, corn is used in different products, such as grits, meal, starch, and syrups, while different crop parts (stalks, grain, and cob) are used in the pharmaceutical industry and for biofuel production. Nowadays, the lignocellulosic part of the corn plant is drawing interest as a raw material for the production of bioethanol, paper, packaging, plywood, cardboard, and many other technical products.

2.1. Composition and use of corn kernel

Corn kernel is composed of four main fractions: the kernel root (tip cap, 1-2%, mainly cellulose), pericarp (hull, 5.5-6%, mainly cellulose), germ (embryo, 10-14%, containing mostly oil, proteins and carbohydrates), and endosperm (82% containing mostly starch, proteins and fats) [20]. Because corn kernels are rich in starch (60–75%), industrial corn production is oriented toward obtaining starch, whereas the germ is treated as a by-product. About 80-84% of the total kernel oil is present in the germ followed by 12% in the aleurone and 5% in the endosperm [21]. The oil content in corn grains can be genetically controlled. After a long selection process, the kernel oil content can be increased by up to 20% [22]. Corn with an oil content level above 6% is designated 'high oil corn'. The corn germ is the most important part of the kernel for oil production. Corn germ contains 35-56% oil, linoleic acid being the most common fatty acid (49-61.9%) [23]. In addition, corn germ contains about 1-3% phosphatides, 1% sterols, and 1.5% FFAs. Nowadays, numerous corn grain products are used in the food, pharmaceutical, chemical, and textile industries; thus, after, processing, there is practically no loss. Corn germ oil is especially important because of its use in human foods and biodiesel production.

2.2. Composition, properties and uses of corn oil

In the corn plant, oil can be found in kernels (seeds), the germ (embryo, a portion of the kernel) and the fiber. Therefore, several terms can be found in the literature, such as 'corn kernel oil' [24], 'corn germ oil' [25] and 'corn fiber oil' [26]. Because of their low oil content, corn kernels and the fiber (about 3–5% and 2–3%, respectively) are used for obtaining the oil at the laboratory scale for research purposes [26]. Oil yields from wet-milled corn germ, dry-milled corn germ and corn fiber by *n*-hexane extraction are 40–50%, 20–25% and 2–3% (based on a dry weight) respectively, while oil yield from ground or flaked whole corn by ethanol extraction is 3–5% [27]. The corn kernel and fiber oils are richer in phytosterols (2–3% and 10–15%, respectively) compared to corn germ oil (about 1%) [28]. Corn oil is commercially obtained from the germ only. The main producers of corn oil are the United States of America, Mexico, Russia, Belgium, France, Italy, Germany, Spain and the United Kingdom [29].

Corn with high oil yield per unit area is behind rapeseed and sunflower [30]. Corn oil yield is about 172 L/ha [31]. The moisture at harvest and drying temperature are the most influential factors affecting the germ oil content and oil yield [32]. Generally, the germ weight and oil yield decrease as the kernel moisture at harvest and the temperature of the drying air increase. Edible oil is obtained from the corn germs from the wet-milling process. Because of its composition and favorable characteristics, corn oil belongs to the group of highquality oils. Containing essential fatty acids and tocopherols, corn oil is of better quality than other edible oils [33]. The composition of corn oil includes both saturated and unsaturated fatty acids such as palmitoleic (11.67%), stearic (1.85%), oleic (25.16%), linoleic (60.60%), linolenic (0.48%), and arachidic (0.24%) [29]. In addition to those, corn oil contains caprylic, capric and myristic fatty acids [34]. It is also rich in vitamin E, which is a strong antioxidant. Corn oil is amongst the richest sources of tocopherols, having reported concentrations of a- and y-tocopherol of 21.3 and 94.1 mg/100 g, respectively [35]. Corn oil is an important component of many foods and has a distinctive taste [36]. Because of its easy digestibility, corn oil has also found applications in medicine. Moreover, recently, corn oil has been used in biodiesel manufacture, especially in combination with ethanol production. Corn oil has an acid value of less than 0.5%, which is a desirable feature with respect to its use in biodiesel production [37].

3. Corn processing to obtain corn meal, germs and DDGS

For the purpose of oil recovery, corn kernel processing can result in three products: corn meal, corn germ, and corn DDGS. The first two products are obtained by milling corn kernels, while DDGS is a by-product of ethanol production from corn, which is separated from whole stillage after fermentation. Corn kernel milling can be performed as dry or wet milling. The dry-milling process is applied in most ethanol facilities because of its high ethanol yield and low capital, energy and water investment, as well as its simplicity. Dry milling may or may not include degerming as a preliminary step. Wet milling combines chemical and mechanical means to afford an endosperm fraction, a germ fraction, and an outer skin (called the bran or hull) fraction. The corn germ fractions from wet- and dry-degerming milling are about 5% and 10% of the kernel mass, respectively [38]. About 50% less oil is recovered by the dry-milling process compared to the wet process [32,39].

3.1. Dry milling

This process, also known as stone grinding, does not fractionate biological components, and the germ is ground along with the other parts of the kernel. It is commonly used to make food products such as corn meal and hominy grits from white corn. These items are basically whole ground corn kernels where the hull and the germ have been slightly removed. It is hard to recover corn oil from ground kernels without using solvents, and solvent extraction is usually characterized by its low efficiency [40].

The dry-degerming process is based on the direct mechanical separation method of the pericarp, endosperm and germ. This technique is simple and less energy demanding than other processes but has low recovery efficiency. The process removes most of the germ and hull from the endosperm, which is oil-free. The most common process of dry degerming, shown in Fig. 1, is the 'tempering-degerming', which involves three main steps [41–43]: short tempering to increase the moisture content, degerming by extrusion, and separation of the different biological components based on size or density. First, the corn kernels are dry cleaned to separate the fines and broken kernels from the whole kernels, which are then washed to remove the surface dirt,



Fig. 1. Dry-degerming milling process (adapted from [43]).



Fig. 2. Wet-milling process (adapted from [46]).

dust, and other extraneous matter. The clean corn kernels are tempered (ca. 15 min) to increase the moisture content up to 20% with hot water (55 °C) and equilibrated for 1–3 h. During this step, most of the outer bran, germ and tip cap are removed, and the endosperm moves through the degerminator to be dried, cooled, and sieved. The bran and germ fractions proceed through the degerminator, where they are dried, cooked and aspirated to remove the bran. Finally, the germ is separated from any remaining endosperm. Compared to the conventional wetmilling process, the dry-determining process separates about 50% less germ [43].

3.2. Wet milling

The wet milling process includes corn soaking (steeping), coarse grinding, degerming, and the separation of the germ from starch (Fig. 2). Steeping is used as an easy way to prepare and separate the kernel portions and technically represents kernel hydration. The water/ kernel ratio, temperature, SO2 concentration, lactic acid and process duration are the factors that mainly influence kernel hydration. Usually, steeping is performed at 48-52 °C for 30-40 h. Then, the corn kernels are coarsely milled in the cracking mills. Attrition mills are usually used for this purpose [44]. Although the objective of milling is to release the whole germ in maximal yield, water must be added to wash the crushed material from the mill teeth and to make a thick slurry. The germ, being less dense, float on the slurry surface and is separated by the blades of the flotation units. In another approach, the slurry is passed through multiple hydrocyclones to obtain an overflow rich in germs and underflow rich in water and other kernel portions [45]. The obtained germ is of high water content and must be dried. Corn germ separation by the wet method is energetically unfavorable and the production cost is high.

Various wet degerming milling processes, which are variations of wet milling, such as Quick Germ [46], Quick Germ Quick Fiber [47–49], and enzymatically milled germ [39], have been developed. If the steeping time and sulfur are dramatically reduced and eliminated, respectively, the process is termed Quick Germ. In another process known as the Quick Germ Quick Fiber process, no chemicals are used during the short period of steeping, and the fiber is separated by flotation after the degerming process. Enzymatic milling (E-Milling) is very similar to the conventional wet milling process except for the partial or full use of the enzymes instead of the inorganic or organic compounds in the steeping stage [50]. This process involves soaking the kernels for 6–12 h, followed by grinding and then incubation with enzymes for 2–4 h. After incubation, the germ and pericarp fiber are separated from the surface by flotation, and the endosperm fiber is



Fig. 3. Scheme of the overall dry-grinding process for ethanol production with co-product streams (WS - whole stillage, WDG - wet distiller grain, TS - thin stillage, CDS - condensed distiller soluble, WDGS - wet distiller grain with solubles, DDGS - distiller dried grain with solubles, and DDG - distiller dried grain).

screened by a sieve. E-milling has passed the concept stage [51] but it has not yet been applied on a pilot or industrial scale because of the high costs of enzymes, the high possibility of microbial contamination during the steeping stage, and the different protein quality and profile obtained during the incubation step.

3.3. Preparation of corn DDGS

In the ethanol production from corn, the obtained whole stillage is further centrifuged to remove excess water (Fig. 3). The remaining solids are known as wet distiller grain (WDG), whereas the liquid phase (called thin stillage) is evaporated to obtain the so called condensed distiller soluble (CDS). The WDG and CDS form a mixture of wet distiller grain with soluble (WDGS), which is, as well as WDG, dried to obtain DDGS or distiller dried grain (DDG). Generally, corn CDS consists of moisture (65%), protein (14%), and oil (20%) based on dry weight, whereas DDGS contains moisture (11%), protein (30–31%), and oil (11–12%) [52].

Considering the composition (8–10% of the oil on dry basis) and annual production (44.2 million metric tons in 2014 and2015 [53]) of DDGS, its significance is underestimated. Currently, DDGS (or DDG) is predominately used for animal feed preparation [54]. The oil content of DDGS is greater than that needed in the feed but, if extracted, it is good feedstock for biodiesel production. Moreover, valuable lipids such as phytosterols, carotenoids, tocopherols, and tocotrienols can be recovered from DDGS oil before its conversion into biodiesel, which is economically favorable [55].

4. Oil recovery from whole ground kernels, germ and whole stillage

Corn oil is recovered from whole ground kernels, germ, and whole stillage. For the first two feedstocks, both mechanical (pressing анд expelling) and chemical (solvent extraction) methods can be applied. Oil recovery from whole ground kernels by cold pressing is not a suitable method because of the very low oil content, the oil remaining (about 4–6%) in the residual press cake, and starch carbonization on the screw press [56]. Therefore, cold pressing is replaced by solvent extraction, which provides a higher oil yield. In fuel ethanol

production, corn oil can be recovered from the germs separated from the corn kernels before fermentation or from the whole stillage after fermentation, which is almost dominant.

4.1. Solvent extraction of corn oil from whole ground kernels

Various solvents, such as n-hexane, acetone, alcohols and supercritical fluids, can be used for corn oil extraction. Because of the health, environmental and safety risk, as well as possible economic reasons, organic solvents are replaced with alcohols, water, and supercritical fluids [57]. The yield and the quality of the obtained oils depend on the solvent type and temperature, as well as the kernel part [58]. The highest corn oil yields from whole ground kernels, the bran and germs are obtained using ethanol as solvent, especially at higher extraction temperatures. Oils are completely soluble in boiling anhydrous ethanol, appreciably soluble (7-10%) in an ethanol/water azeotrope at its boiling point and poorly soluble at lower temperatures [59]. Anhydrous ethanol has been used for oil extraction from ground kernels in batch and multiple-batch processes [60]. The optimized batch process has been shown to have a yield of 3.3 g oil/100 g. The multiple-batch process consists of three stages performed at the optimal conditions of the single batch extraction employing two modes: fresh corn with recycled ethanol and recycled corn with fresh ethanol. In the first mode, the oil yield decreases at each successive stage because of the passage of moisture from the corn to ethanol. In the second mode, the oil yield decreased significantly after the first stage, but the total yield reached about 4.5 g/100 g (93% extraction efficiency) after three extraction stages.

Sequential ethanol extraction from flaked whole corn kernels is a promising multipurpose process for the simultaneous corn oil extraction and drying of ethanol, protein extraction, and ethanol production from corn starch for upstream extraction after distillation [59]. The oil extraction method involves seven-stage percolation with countercurrent ethanol flow performed at 75 °C and a solvent-to-corn mass ratio of 2:1. Using this method, the obtained corn oil yield is greater than 90% of the oil content, whereas the oil yield obtained by *n*-hexane extraction is only 72%. The additional advantage of this process is the adsorption of the moisture from ethanol by the flaked corn, thus allowing the production of > 99% ethanol.

4.2. Corn germ oil recovery

For the extraction of oil from corn germs, pressing, extrusion, and extraction with an organic solvent, aqueous, aqueous enzymatic or supercritical fluid have been used (Fig. 4). Each extraction method has benefits and drawbacks that are briefly summarized in Table 1. The quality and amount of corn oil depend on the applied extraction method.

At present, many oil factories use the pressing method for oil recovery from corn germs although the obtained oil yield is only 65% [61]. To achieve higher oil yields, the treatment of the seeds before pressing and pressing followed by solvent extraction has been used. The oil yield from corn germs depends on factors such as the type of preheating, moisture content, temperature, screw speed, and nozzle diameter. To increase the oil yield, heating the corn germs in a conventional (at 180 °C) or microwave (at 1500 W and 2450 MHz) oven can be carried out. Microwave heating is more suitable for dry-milled germ, providing an oil yield of 7% after 4.5 min, whereas conventional heating for 5 min provides the maximum oil recovery from wet-milled germ (about 22% oil). Oil recovery by pressing is also influenced by the moisture content of the corn germ [62]. For example, in the range of initial moisture contents studied (15-20%), the oil recovery increased with increasing moisture content. The highest oil recovery (65%) was achieved from the corn germ with up to 6.5% moisture. Furthermore, corn germ with < 2% moisture became overheated during the pressing process, causing a reduction in the oil yield or even burning in extreme



Fig. 4. Schematic presentation of corn germ oil recovery by pressing (a), solvent extraction (b), enzyme-assisted aqueous extraction (c), and supercritical fluid extraction (d).

cases. Therefore, extrusion has been suggested as a corn germ pretreatment method before solvent extraction [63]. This process replaces crushing, drying, flaking, cooking, and pre-pressing. Under the optimal extrusion parameters, this method provides a much smaller amount of residual oil (0.61–0.66%) compared to pressing alone and the combination of pre-pressing/*n*-hexane extraction (5–6% and about 2%, respectively). Various organic solvents and water have been used for the extraction of corn germ oil. The most common commercial process for obtaining oil from corn germ is extraction by n-hexane because of its high extraction efficiency and low process cost. Under the same extraction conditions, n-hexane and *iso*-heptane act as better solvents than heptane [64]. Moreau et al. [65] extracted oil from dried wet-milled corn germ with or without homogenization using n-hexane at room

Table 1

Comparison of various extraction methods for obtaining corn oil.

Methods	Advantages	Disadvantages
Pressing	Simple, safe and useful for feedstocks with low oil content Convenient for high capacity	Remaining the oil in the oily press cake Low oil yield Frequently stripping and cleaning of the screw press High energy requirements
<i>n</i> -Hexane solvent extraction	Efficient High oil yields Suitable for sources with high and medium oil content	Environmentally unsuitable Non safety Potential health risks Significant capital and operational investments Low quality of oil
Ethanol solvent extraction	Effectiveness Oil and meal oil of very good quality Suitable for oil recovery from co-product of dry-grinding ethanol producers	Higher pressure and temperature above the ethanol boiling temperature Expensive and hazardous equipment Unsuitable for continuous process
Aqueous extraction	Economical and environmentally favorable ("green" process)	Inefficiency Low quality of oils Unpleasant oil odor
Enzyme-assisted aqueous extraction	Mild reaction conditions Low operational cost High oil yield Very good quality of the oil Environmentally auspicious, safety and no health risks ("green" process)	High price of the enzymes
SC-CO ₂ extraction	Safe, not toxic and explosive High quality oils Good oil yields Low cost and easy availability of CO ₂ Simple removing from the extraction products	Expensive equipment for high pressure High capital and operational costs

temperature for 1 h. A significantly higher oil yield (42.7 \pm 2.0% of the oil in germ) was obtained from homogenized corn germ rather than from the non-homogenized germ (3.6 \pm 0.2%).

Ethanol is commonly used for oil extraction from whole ground kernels [59,60]. The water-ethanol solution, as an efficient de-emulsifier, allows free oil to be obtained, thus simplifying the downstream process and shortening the overall extraction time. Oil extraction with aqueous ethanol (30%) is commonly carried out from dry milled corn germ at elevated temperatures (over 60 °C). At a solid-to-solvent ratio of 1:7 g/mL, a higher oil yield (94.05 \pm 0.32% of the total germ oil) has been obtained at 70 °C compared to 60 °C for 2 h [23]. The pretreatment of corn germ by steam explosion or citric acid soaking followed by steam explosion increases the aqueous ethanol extraction efficiency [23]. Under the extraction conditions applied for the untreated germ, the oil yield from the steam-exploded corn germ increased to 88.51%. Corn germ soaking with citric acid (0.05 M) for 2 h at a solid-to-liquid ratio of 1:2 (w/v), followed by steam explosion results in an oil yield of 93.74%. The increase in oil yield has been attributed to the hydrolysis of the cellulose and hemicellulose contained in the cell wall by citric acid and the mechanical effect of fast compression and decompression, which destroys the oil-protein complexes and releases the oil. Using a surfactant is another approach for improving oil extraction from corn germ [66]. The mechanism of oil extraction by a surfactant is based on the decrease in the interfacial tension between the extraction agent and oil. With the addition of anionic extended surfactants (sodium linearalkyl polypropoxylated polyethoxylated sulfates) in the presence of NaCl (0.4% and 1%, respectively), an oil yield above 80%, based on the total germ oil yield, has been achieved at about 25 °C for 45 min extraction time.

From an economic and ecological point of view, water is the most valuable extraction agent. Moreau et al. [65] took dried wet-milled corn germ, treated it with a buffer, ground it and finally cooked it in boiling water for 20 min. Subsequently, the mixture was churned at 65 °C for 20 h in a rotary incubator/shaker (160 rpm), cooled and centrifuged to separate the oil on the mixture surface. The oil yield was 15.3 \pm 0.4% corresponding to 36.6 \pm 1.1% of the yield achieved by *n*-hexane extraction. A similar process has been applied in the case of aqueous oil extraction from dried wet-milled corn germ [67]. The main differences are a higher cooking temperature (101–122 °C), higher incubation temperature (72 °C), and longer incubation time (24 h), as well as freezing in the centrifuge for efficient oil separation. In this process, the highest oil yield was about 40% of that extractable using *n*-hexane.

The enzymatic pretreatment of corn germ has recently emerged as a novel and effective method of improving the oil yield by cold pressing and aqueous extraction techniques. This method, known as aqueous enzymatic extraction (AEE), provides an oil yield twice as high as that achieved via aqueous extraction under similar extraction conditions. AEE includes the reduction of germ particles in a buffer solution, pH adjustment, and enzyme addition, followed by incubation, churning, and oil recovery. The limitations of AAE for commercial applications are related to the enzyme type, the amount of enzyme required, and the cost of the enzyme, as well as the requirement of different pretreatments and unrecovered emulsified oil.

Mixtures of different enzymes classes are frequently used, such as cellulase, xylanase, amylase, pectinase and protease [68]. The highest oil yields (78–82%, relative to *n*-hexane extraction) were obtained by using three commercial *Trichoderma reesei* cellulases [65]. Oil recovery increased up to about 90% after the fourfold scale-up of the process. Aqueous and AEE extraction from dried wet-milled corn germ using commercial cellulase provided the highest oil yield after cooking the germ-buffer mixture at 122 °C, followed by incubation at 70 °C for 22–24 h and shaking at 160 rpm [67]. The oil yield obtained by the AEE method (72%) was twice that achieved by aqueous extraction. The advantage of this process is the use of equipment for processing larger germ amounts, which can be scaled up to a typical dry grinding plant.

AEE was first used for oil recovery from the wet-milled germ containing 40-50% of oil and a high oil yield has been achieved [69]. On the other hand, the AEE method is not efficient for dry-fractionated germ containing 15-20% oil. Different pretreatments have been applied to increase the oil yield from the dry-fractionated germ by AEE, such as germ grinding and cooking before AEE [70]. Because of the germ dryness, microwave irradiation is suitable for germ heating. The pretreated germ is mixed with water, cooked under pressure, milled, and incubated with commercial cellulase at 50 °C for 24 h. The foam fraction of the dispersion, which contains oil, is collected and centrifuged to separate the oil. In this process, the highest oil vield achieved is 49% (based on the total oil content) after germ pretreatment, including milling and vacuum drving before heating [70]. However, a significant amount of oil (about 36% of the total oil content), known as fine oil, remains in the aqueous fraction of both the dispersion and the foam and cannot be separated by centrifugation. A positive effect on the oil yield can also be achieved by treating the germ dispersion with commercial α -amylase and glucoamylase before treatment with the AccelleraseTM 1000 cellulase [71]. By applying the best extraction procedure, the obtained oil yield was 61.5% of the n-hexane-extractable yield.

AEE has been used to recover oil from commercial dry-milled corn germ (about 15-20% oil based on the dry germ weight) and corn germ using a novel enzymatic wet-milling process, known as E-Germ (about 40-50% oil, based on the dry germ weight) [26]. No oil was produced from the dry-milled corn germ by combining cellulase with the procedure developed for wet-milled corn germ. However, after the pretreatment of corn germ by boiling in a buffer for 30 min or microwave irradiation before cellulase extraction, the oil yields were significant (up to 56.6% and 42.6%, respectively). To increase the oil yield, a twostep process that includes the treatment with acidic cellulase and alkaline protease has also been developed. The obtained oil yields from dry-milled corn germ and enzymatically treated corn germ (E-Germs process) are 50-65% and 80-90%, respectively. The advantage of this two-step process is the elimination of germ cooking or drying, thus reducing the energy costs. In another aqueous method [72], the protein and oil yields have been improved by water steeping and wet fractionation of dry-milled corn germ. Using this two-step incubation process, the highest oil yield with respect to the initial oil content was 72%.

The most commonly used supercritical fluid is CO_2 because of its excellent critical parameters (31.1 °C and 7.38 MPa) for extracting thermally sensitive compounds [73]. The ability of CO_2 to extract the desired compounds results from its low viscosity and high density that allow penetration into solids and easy solubility, respectively [74]. The major advantage of the supercritical CO_2 (SC-CO₂) extraction is the high quality of extracted oils that are clear and have a unique aroma and flavor. The oil yield and efficiency of SC-CO₂ extraction from some oil-bearing materials can be improved by cold pressing of the oily material before the extraction [75] or by coupling ultrasonication and SC-CO₂ extraction [76]. SC-CO₂ extraction of corn germ oil is commercially used by the MOR Supercritical LLC Company (USA) [77].

Wet-milled corn germ should be ground to allow good contact between phases but should not be too fine to avoid particle concretion [78]. The highest oil yield (97–99% of the total recoverable oil) has been obtained at pressures and temperatures of 30–33 MPa and 42–60 °C, respectively. Furthermore, Bebić et al. [79] reported excellent oil recovery from wet-milled corn germ an oil residue in the extracted meal of 0.9%. SC-CO₂ oil extraction from wet-milled corn germ can be improved in the presence of ethanol as a co-solvent [80]. For example, the obtained oil yield in the presence of the optimal ethanol amount of 10% is about 50%, based on the mass of dry corn germs at a CO₂ consumption of less than 20 kg/kg of dry corn germ.

4.3. Corn oil recovery from whole stillage

DDGS is the most frequently used feedstock for corn oil recovery, whereas whole stillage and CDS are very rarely used. Oil is commonly

Table 2 A review of the transesterificati	on reactions of differ	ent corn oil-based feedstock	S.						
Type of reaction	Feedstock	Type, volume of reactor, mL	Type of acyl	Alcohol: oil molar	Catalyst / loading,% to the oil	Temperature, °C	Optimal reaction con	ditions	Reference
		/ Type of agitator, agitation intensity, rpm	acceptor	ratio, mol/mol			Reaction conditions	Yield (Conversion), % / Time, h	
Homogeneous base catalysis	Corn oil Corn oil	Cylinder, 10 / shaker, 156 Autoclave, 100 / mechanical	Methanol Methanol	6:1 14:1	KOH / 0.1–1 NaOH / 0.3	25 60	1%	(100) ^a / 0,33 (79.8) / 1	[87] [88]
		/ 800	Ethanol		NaOCH ₃ / 0.3 NaOH / 0.3 NaOCH / 0.3			(99)/1 (84.7)/1 (036)/1	
	CDO, without		Methanol		NaOH / 0.3			(3.7)/1	
	pretreatment		Ethanol		NaOCH ₃ / 0.3 NaOH / 0.3 NaOCH / 0.3			(72.4) / 1 (16.4) / 1 (02.6) / 1.67	
	CDO, pretreated		Ethanol		NaOCH ₃ / 0.3			(84.1)/ 1.67	
	tor impurities CDO, pretreated		Methanol		NaOCH $_3$ / 0.3			(93.8) / 1	
	for FFAs		Ethanol	1.2	NaOCH ₃ / 0.3	c,		(94.4) / 1.5	51
	Corn oil. refined		Metnanoi Ethanol	0:1	NaOCH ₃ / U.5 KOC ₂ H∈ / 0.5	60 75		90 / 1 79 /2	[4]
	Corn oil	-/155	Methanol	3:1-6:1	NaOH / 0.3-0.6%	50-65	6:1, 0.5%	95 / 0.25	[89]
	Corn oil, heated 9 h	шlod- ЕОО /	Mathemal	5.0	NoOII (0 E 1 9E	09 89	6:1, 0.7%	85 / 0.25 67 / 1 F	5
	EFA)	riask, auu / -	INTELNATION	2:1	C2.1-C.U / HUBN	02-02	U./ Э% NAUH, 1% FFA	C.I / 16	[C]
	Corn oil	Tank, 500 / magnetic, 600	Methanol	6:1	KOH / 0.8–1.2	30-63	1.1%, 55 °C	98.75 / 1	[06]
	Corn oil Corn oil	-/ultrasonic (150–450 W) Membrane reactor, 480,	Methanol Methanol	6:1 -	KOH / 1 NaOH / 0.5	30-70 65	55 °C, 450 W	91.2 / 1 -	[91] [92]
		630, 740 / - B-:::- 500 /	111						[00]
	Corn oil	botue, 500 / magnetic, 60	Metnanol Ethanol	0:1	KOH / I	60 75		83.5 / 2 71.1 / 2	[93]
	Corn oil	Vessel, 250 / ultrasonic	Ethanol	4:1-5:1	NaOH $/$ 0.007–0.013 ^b	28	4.5:1, 0.01%	62.9 / 0.5	[94]
	Corn oil	-	Ethanol	10:1-12.4:1	KOH, NaOH / 1.4–1.88	35-55	11:1, KOH,1.6%	93.14/-	[95]
	Corn oil	I	Methanol	3:1-12:1	KOH/ 0.25-1.5	40–70	9:1, KOH, 1.1%, 60 °C	I	[96]
					NaOH / 0.25–1.5		9:1, NaOH, 0.9%, 50 °C	I	
	Corn oil	1	Methanol		KOH / 4–6	30-60	5%	97 / 2	[67]
Homogeneous acid catalysis	Corn oil	-/ultrasonic (240–360 W)	Methanol	5:1-11:1	Ionic liquid / 5–11	70-100	1:11, 11%, 90 °C, 360 W	(91.85) / 0.83	[86]
	Corn oil	Microwave	Methanol	2.5:1 ^c	$DPAM^d/5-20^e$	150	20 ^e	$100 \neq 0.33$	[66]
					DPABS/5-10 ^e DDAT/2-10 ^e		10 ^e 5 ^e	96 / 0.33 100 / 0 33	
		Reflux			DPAM/ 5-20 ^e	65	20°	100 /24.5	
	Corn oil	Rottle	Methanol	30-5 î	DPAT/1 ⁻ H ₋ SO - conc /0 3 ^g	59		10 / 24 (70 0) / 12	[100]
	Corn oil	Autoclave, 400 / propeller,	Ethanol	3:1-24:1	H_2SO_4 / 0.02–0.1	155-195	24:1, 0.06%, 175 °C	(100) / 4	[101]
	CDO (with 1–6%	300 Flask, 500 / -	Methanol	8:1	${ m H_2SO_4}$ / 0.5–1.25	68–69		20 / 4	[5]
In situ acid catalyzed trans-	Whole corn kernels	Bottle	Methanol	30:5 ^f	H_2SO_4 , conc./0.3 ⁸	65		(50.1) / 12	[100]
esterincation	(M-F-T) Whole corn kernels							(67.0) / 12	
	(M-T-F) Whole corn kernels (S-T/F)							(70.9) / 12	

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(continued on next page)

Table 2 (continued)									
Type of reaction	Feedstock	Type, volume of reactor, mL	Type of acyl	Alcohol: oil molar	Catalyst $/$ loading,% to the oil	Temperature, °C	Optimal reaction con	ditions	Reference
		/ 1ype or agitator, agitation intensity, rpm	acceptor	rauo, mot/mot			Reaction conditions	Yield (Conversion), % / Time, h	
Two-step acid/base process with an intermediate neutralization step	CDO (with 1–7% FFA)	Flask, 500 / -	Methanol	8:1	H ₂ SO ₄ (0.5)/ base neutralization/ NaOH (0.25–1%) H ₂ SO ₄ (0.5)/ ion-exchange	68-69	1% NaOH, 1% FFA 0% FFA	95 / 1.5 98 /1	[2]
Heterogeneous base catalysis	Corn oil	Batch reactor - / - 800 (500 kPa)	Methanol Ethanol	12:1	neutralization / NaOH (U.5) ZnAl ₂ O ₄ / -	150–200	7% FFA 150 °C 200 °C	98 / 1.5 (22.7) / 2 (32.5) / 2	[88]
	Corn oil Corn oil	Flask, 150 / magnetic, 800 Flask, - / magnetic, -	Methanol Dimethyl	10:1 - 30:1 3:1 - 9:1	MgU / 2–9 ZnO / 2–11 KOH, solid / 10–20	65–75	ZU:1, 5% 15:1, 9% 9:1, 16.3%, 60 °C	62.61 / 10 53.1 / 10 90.9 / 9	[102]
	Corn oil Corn oil WFCO	Flask, 250 / -, 600 Flask, 250 / - Flask, 250 / magnetic, 900 Flask, 250 / magnetic, 200	carbonate Methanol Methanol Methanol	16:1 12:1 6:1-12:1 6:1-12:1 6:1	CaO/SiO ₂ / 6 CaO/SiO ₂ CaO/Y-Al ₂ O ₃ / 6 CaO/Y-Al ₂ O ₃ / 1–5 CaO from snails shells / 3–9 CaO 7 3%	50-65 65 60 -65 60	60 °C 12:1, 5%, 65 °C 6:1, 3% 	(85.6) / 8 79.1 / 5 (91.58) / 6 96 / 1 95 / 1	[104] [105] [106] [107]
Heterogeneous acid catalysis	Corn oil Corn oil	vesseı, 500 / mecnamcaı, 500 Flask, 100 / -	Methanol	3.4:1 - 12.6:1 4:1-40:1	ba(UH)2 / 1./0-4.24 Organotin(IV) carboxylates / 0.01_0.05	33 65	11.32:1, 3.0% 32:1, 0.05	2 / 21.66	[109]
Enzymatic catalysis	Corn oil	Bottle, 500 / magnetic, 60	Ethanol, absolute Absolute ethanol Ethanol, 96%	3:1 6:1	Lipase from Th. laruginosa on silica / 2.8	35		91 / 24 98.9 / 12 94 / 24 74 8 / 24	[93]
	Corn oil WFCO	Batch (SC-CO ₂ ^k), 10 / magnetic Flask, 250 / magnetic, 200	Methanol Methanol	3:1-9:1 6:1	Lipase from C. <i>antarctica</i> (Novozym 435) on acrylic resin / 5–15 Lipase from C. <i>antarctica</i>	40–60 60	6:1, 15%, 60 °C, 10 MPa -	87./1	[110] [107]
	CDO	Flask, - / shaker, 150	Dimethyl carbonate	2:1–20:1	(Novozym 435) / 3 Lipase from C. <i>antarctica</i> (Novozym 435) on resin / 10–30	45–65	15:1, 20%, 60 °C	91.0 / 18	[111]
	Corn oil	Continuous SC-CO ₂ packed- bed reactor, 11–35 MPa	Methanol	1:0-1:1	Lipase from C. <i>antarctica</i> (Novozym 435) on acrylic resin / 0.4–3.6 L/min	35-63	7:1, 62.9 °C, 19.4 MPa, 0.72 mL/ min SC-CO ₂	93.3	[112]
Non-catalytic supercritical process	Corn oil	Autoclave, 100	Methanol	6:1-41:1	1	202–287	41:1, 287 °C	98 / 0.083	[67]

^a In the presence of dimethyl ether as co-solvent.
 ^b Molar ratio.
 %.
 ^d DPAM - diphenylammonium mesylate, DPABS - diphenylammonium benzenesulfonate and DPAT - diphenylammonium tosylate.
 ^e mol.%.
 ^f mL/g.

⁸ mL.

^h LL corn variety; M-F-T - milling, fermentation and transesterification, M-T-F - milling, transesterification and fermentation; and S-T/F - separation followed by transesterification and fermentation. In the presence of diethyl ether as co-solvent.

^j Weight ratio.

k SC-CO2 - supercritical CO2.

recovered from DDGS using a solvent [5,81] or SC-CO₂ [82,83] extraction. Ethanol extraction of corn oil from DDGS at the optimum ethanol-to-DDGS ratio of 6 mL/g, 50 °C and under agitation for 30 min has been shown to yield 66 mg oil/g DDGS, corresponding to 50% of the total oil content in DDGS [81]. The application of *n*-hexane is especially useful for the oil extraction from whole stillage with low oil content [5]. Oil extraction from whole stillage and CDS at an optimal *n*-hexane-to-substrate ratio of 0.20 g/g provided oil yields of 9.8 \pm 0.6% and 12.0 \pm 0.8%, respectively. Similar corn oil yields (12.7% and 12.5%, respectively) have been obtained from DDGS by *n*-hexane extraction for 24 h and SC-CO₂ extraction at 55 MPa, 80 °C and 2 L CO₂ /min for 60 min [82]. The largest oil yield of 9.2% (82% of oil yield obtained by Soxhlet extraction with petroleum ether for 5 h) has been obtained from DDGS by SC-CO₂ oil extraction at 49.6 MPa and 70 °C for 340 min [83].

4.4. Optimization and kinetics of corn oil recovery

Although the optimization of the process parameters for corn oil recovery is particularly important for increasing the oil yield, improving the oil quality, and reducing the operational costs, it is rarely employed. The optimization of corn germ extrusion pretreatment has revealed a significant influence of the screw speed and temperature, as well as the interactions of the material moisture-nozzle diameter, material moisture-screw speed and screw speed-nozzle diameter, on the residual oil content [63]. The optimal extrusion parameters resulted in a residual oil content of 0.61–0.66%. Kwiatkowski and Cheryan [60] optimized the oil recovery from whole ground corn kernels and found the most significant influence of ethanol concentration on the oil yield, followed by the solvent-to-solid ratio and their linear interaction. The oil yield was 3.3 g/100 g (extraction efficiency of 70%) under the optimal extraction conditions. The same oil yield was obtained using 95% ethanol and a solvent-to-solids ratio of 8 mL/g. Fewer studies have aimed to optimize the oil recovery from corn germ [63. 78, 79, 84] and ethanol production co-products [5,87]. However, an increase in the solvent-to-substrate ratio in the range from 0.03 to 0.20 g/g in *n*-hexane oil extraction from whole stillage and CDS has been shown to lead to an increase in the extracted oil yield, but further increases have no significant effect [5]. SC-CO₂ oil extraction is more frequently optimized [5,78,79,83,84]. At a constant extraction temperature, the oil yield from wet-milling corn germ increases as the extraction pressure increases [79]. Under the optimal extraction conditions (490 MPa and 50 °C), the oil yield is 97% of the total oil content [94]. Similarly, an increase in both the pressure and temperature for SC-CO₂ oil extraction from milled corn germ results in an increase in the extraction rate, but the effect of the temperature is more noticeable [84]. The flow rate of the SC-CO₂ has an insignificant effect on the oil yield, suggesting that external mass transfer does not control the extraction process. Thus, smaller particle sizes should not be used in SC-CO₂ extraction of ground wet-milled corn germ because of the high specific solvent consumption [78]. Under the optimal extraction conditions, an oil yield of 97–99% (based on the total recoverable oil) has been obtained. The extraction time has a significant effect on oil yield, particularly at the beginning of the extraction. For SC-CO₂ oil extraction from DDGS, the optimal extraction conditions were experimentally determined to be 49.6 MPa and 70 °C, for which the obtained oil yield was 9.2% after 340 min [83].

Mathematical modeling of corn oil extraction has been very rarely employed. There are no studies concerning the modeling of corn oil extraction from whole ground corn kernels and corn germ using pressing, solvent extraction, or AEE. Only a few studies have dealt with the modeling of SC-CO₂ extraction from corn germ and DDGS. Rónyai et al. [80] modeled the oil extraction rate from dry corn germ by SC-CO₂ in the presence of ethanol as a co-solvent. Rebolleda et al. [84] used the model proposed by Sovová [85] to describe the experimental data of SC-CO₂ oil recovery from corn germ. According to this model, the extraction curves are composed of two parts: the first corresponds to the initial extraction period when the easily available oil is immediately transferred to the fluid phase, and the second corresponds to the final extraction period, when the oil first diffuses through the plant material and afterwards to the fluid phase. However, after investigating SC-CO₂ oil extraction from DDGS, Ciftci et al. [83] concluded that the extraction curves consist of three periods. In the first period, the extraction rate is constant, the easily available oil is quickly extracted and the mass transfer is controlled by the limitations in the solvent phase. The extraction rate rapidly decreases in the second period because of the reduced oil availability. In the last period, the extraction is very slow because of the lower availability of oil and the diffusion limitations. They applied the Sovová model [86] in the description of oil extraction of the extracted oil amount in the three regions.

5. Biodiesel production from corn-oil-based feedstocks

The transesterification reaction is the most frequent method used for the conversion of TAGs from corn oil-based feedstocks into biodiesel such as neat corn oil, WFCO, and CDO. Table 2 summarizes the optimal reaction conditions for both catalyzed and non-catalyzed transesterification reactions of different corn-oil-based feedstocks, and Fig. 5 shows schematically possible transesterification methods for biodiesel production from corn-oil-based feedstocks.

5.1. Transesterification of corn oil

5.1.1. Homogeneously catalyzed transesterification

The homogeneously catalyzed transesterification of corn-oil-based feedstocks is commonly performed as a one-step process in the presence of base catalysts (alkali hydroxides or alkoxides), whereas acid catalysts (sulfuric acid and acid ionic liquids) are rarely used (Table 2). Sodium methoxide has proven to be a better catalyst than NaOH for the transesterification of corn oil with methanol or ethanol at 60 °C because it ensures a higher TAG conversion (> 90%) [90]. On increasing both the NaOH amount to 0.5% and the methanol-to-oil molar ratio (MOMR) to 6:1, the neat corn oil conversion to methyl esters increases linearly, although a very small change to the ester yield has been observed in the range 50–65 °C [89]. Under the optimal reaction conditions, the best ester yield achieved was 95% after 15 min. Demirbas [97] obtained biodiesel yield of 97% from corn oil using 5% KOH.

Methanol and ethanol are usually used at a temperature close to or below their boiling points, except for acid-catalyzed transesterification under pressure [101] and ultrasonication [98]. In general, lower MOMRs are used with base (3:1–14:1, most frequently 6:1) than with acid (3:1–24:1) catalysts. Higher conversion of corn oil has been achieved with methanol than with ethanol and KOH [110] or NaOCH₃ [105] under the same reaction conditions, whereas the opposite result has been observed with NaOH [88].

Until now, only H_2SO_4 and a few ionic liquids have been used as acid catalysts in transesterification of corn oil. The use of acid catalysts might result in a high conversion of corn oil. The complete conversion of corn oil with ethanol has been achieved in 4 h in the presence of trace H_2SO_4 as a catalyst at 175 °C and an ethanol-to-oil molar ratio of 24:1 [101]. However, the presence of water (< 3%) in the reaction mixture dilutes the trace amount of H_2SO_4 , thus slightly reducing the reaction rate. Furthermore, when a higher FFA amount is present in the system, a lower final esters yield is obtained. A high biodiesel yield (up to 100%) can be achieved from corn oil with acid ionic liquids [98,99].

5.1.2. Heterogeneously catalyzed transesterification

The most frequently used heterogeneous (solid) catalysts for corn oil transesterification are alkali- and alkaline earth metal oxides and hydroxides (Table 2). The catalytic activity of solid catalysts depends on their nature and preparation method. Neat base (MgO, ZnO, Ba(OH)₂, ZnAl₂O₄ and solid KOH) [88,102,103,108] and loaded (CaO on silica or



Fig. 5. Schematic presentation of the transesterification of corn oil-based feedstocks: homogeneously catalyzed (a), heterogeneously catalyzed (b), enzymatically catalyzed (c), and non-catalyzed (d) reactions.

alumina) [104–106] catalysts are mainly used. However, CaO from a natural source (snail shells) has also been employed [107]. The only examples of new solid acid catalysts are organotin(IV) carboxylate complexes [108]. Methanol and dimethyl carbonate (DMC) have been used as acyl acceptors in a wide range of the acyl acceptor-to-oil molar ratio (3:1–12:1 and 4:1–40:1 for solid base and acid catalysts). Generally, the reaction temperature is close to the boiling point of the acyl acceptor or lower, except reactions conducted at a high pressure and temperature (150–200 °C) [88]. Usually, the ester yield is lower and the reaction duration time is longer than for homogeneous catalysts. The best ester yield (> 96%) from neat and WFCO has been achieved with Ba(OH)₂ [108] and CaO from snail shells [107] within 2 and 1 h, respectively.

When MgO and ZnO are used as catalysts, oil conversion starts to increase above the critical MOMR (20:1 and 15:1, respectively) [102]. The ester yield increased with increasing catalyst loading, but MgO was more effective than ZnO, which was attributed to the greater effective reaction surface of the smaller, more uniform MgO particles. Much lower conversions (between 22% and 33%) were achieved in corn oil transesterification with methanol and ethanol over ZnAl₂O₄ at 150 and 200 °C, compared to the conversion in the presence of NaOH or NaOCH₃, probably because of mass transfer limitations [88]. The optimum biodiesel yield of 99.15% was reached in 2 h in corn oil transesterification over Ba(OH)2 in the presence of diethyl ether as a cosolvent [108]. However, the authors did not recognize the contribution of homogeneous catalysis [113]. Only Sun et al. [103] studied the transesterification of corn oil with DMC instead of methanol and solid KOH as a catalyst when the maximum esters yield (90.9%) was obtained in the boiling reaction mixture for 9 h.

Moradi et al. obtained oil conversions of 85.6% [104] and 79.1% [105] within 8 and 5 h and using 70% CaO/SiO₂ and 40% CaO/ γ -Al₂O₃ catalysts synthesized by sol-gel and impregnation method, respectively. In both the cases, the catalysts could be used five times with the esters yield decreasing with each catalyst reuse, because of the leaching of CaO by methanol, which was more prominent in the case of the catalyst prepared by impregnation. The oil conversion degree increased with increasing of loading of CaO onto the γ -Al₂O₃ support, MOMR, catalyst concentration, temperature, and stirring speed [106]. A aigh MOMR of 32:1 and a long reaction time of 48 h were required to achieve an 83% conversion of corn oil into biodiesel using organotin(IV) carboxylate complexes as new environmentally friendly solid catalysts [109].

5.1.3. Enzymatically catalyzed transesterification

The lipases from *Thermomyces lanuginosa* [93] and *Candida antarctica* (Novozym 435) [110––112, 114] immobilized on either silica or resin have been used in corn oil transesterification in previous years (Table 2). Methanol, ethanol or DMC as the acyl acceptor and the lipase amount of 3–20% were applied at 35–65 °C. Batch stirred reactors are commonly used, although continuous SC-CO₂ packed-bed bioreactor may also be used.

Mata et al. [93] conducted the transesterification of corn oil with ethanol (absolute, 96% and 70% v/v) in the presence of the *T. lanuginosa* lipase at 35 °C. The highest esters yield (98.9%) was achieved with absolute ethanol for 12 h. The presence of water in the ethanol reduced the ester yield, and this reduction increased with increasing water concentration. The optimization process using the response surface methodology (RSM) showed that higher reaction yields are obtained for a shorter time (12 h) and at a lower temperature (35 °C rather than 45 °C). An excess of enzyme (above 2.5%) did not promote the reaction. However, higher alcohol-to-oil molar ratio (6:1 instead of 3.1) gave a higher ester yield. The enzyme was reused four times under the optimum reaction conditions with esters yield decreasing to 70.8% because of the catalyst loss during filtration, washing, and drying. The enzyme proved to be a better catalyst than KOH, regardless of the type and concentration of alcohol.

The esterification/transesterification of CDO with DMC has been carried out with Novozym 435 as a catalyst in the presence of various sorbents, such as acrylic resin, 4A-molecular sieve, blue silica-gel or tert-butanol, as water removal agents [111]. Only the acrylic resin proved to be a good adsorbent for the removal of both, water inherent to the used oil and water generated during the esterification of FFAs and DMC. When the DMC-to-oil molar ratio increased, the ester yield increased rapidly and then slightly decreased, because of the excess of DMC diluted in the oil, which reduced the contact between the oil and lipase as well as the collision frequency of the resin. When the temperature increased from 45° to 60 °C, the ester yield started to increase to the maximum value, but the ester yield decreased at 65 $^\circ \mathrm{C}$ because of the denaturation of the lipase. Furthermore, the ester yield increased with increasing lipase concentration up to only 20%, whereas no increase in the ester yield was observed at higher catalyst amounts. Finally, Novozym 435 combined with a polymer resin showed excellent operating stability without losing any catalytic activity after eight repeated cycles. Ciftci and Temelli [110,112] used RSM to optimize the use of the lipase Novozym 435 immobilized on an acrylic resin for the

conversion of corn oil into biodiesel in both batch and continuous SC- CO_2 reactors. Continuous bioreactors are more favorable than the batch reactors because of their higher cost effectiveness as a consequence of the enhanced lipase stability, facilitated lipase reuse, higher lipase-to-oil ratio, and ease of operation.

5.1.4. Non-catalytical supercritical transesterification

Only Demirbas [97] has so far studied biodiesel production from corn oil and supercritical methanol, finding that increasing the supercritical methanol temperature from 748 K to 833 K (i.e. 475–560 °C) improves the ester yield significantly. At a high methanol-to-oil molar ratio of 41:1, a 98.3% ester yield was achieved within 5 min, and the biodiesel purity was also high (99.6%). This process can compete with the KOH-catalyzed process where an ester yield of 97% was obtained after a significantly longer reaction time (2 h).

5.2. Transesterification of other corn-based feedstocks

Apart from corn oil, waste frying and CDO are used for biodiesel production via transesterification. However, the processes based on these feedstocks have been rarely studied.

To date, only El-Gendy et al. [107] has reported biodiesel production from WFCO using a catalyst obtained by the calcination of waste snail shells at 800 °C. The savings obtained by using WFCO for biodiesel production can be illustrated by the amount that commercial companies charge for the disposal of this waste, which is currently about 0.26 US \$/L [115]. The catalytic activity of the used catalyst (basically CaO) is comparable to that of neat CaO and immobilized lipase (Novozym 435). Under the optimal reaction conditions, a biodiesel yield of 96% is obtained in 60 min, which is comparable to the ester yield of 95% obtained over neat CaO and much larger than the yield achieved over Novozym 435 (87%). Unfortunately, no data were given on the reusability and calcium leaching of this catalyst originating from the natural source. Khan and Dessouky [89] investigated NaOH-catalyzed biodiesel production from thermally-treated corn oil. They found that, for increases in the catalyst concentration of up to 0.7%, the oil conversion increased linearly. A linear increase in the ester yield was observed with increasing MOMR. A higher ester yield for the same reaction time and the lower catalyst amount was obtained with neat corn oil, compared to the use of the same oil heated for 9 h (95% versus 85% in 15 min) [89]. They explain that this result arises from the reduction in the catalyst amount by reaction with the FFAs in the heated corn oil. In addition, as in the case of neat corn oil, the ester yield changed very slightly with increasing temperature from 50 to 65°C.

Despite its possible benefits, CDO has been used for biodiesel production in only a few studies [4,5,88]. Because of the high FFA content, CDO is used for biodiesel production in a two-step process consisting of the acid-catalyzed esterification of FFAs and base-catalyzed transesterification of acid-pretreated CDO. Both reactions are conducted under total reflux conditions. In the first step, H₂SO₄ is commonly used as an acid catalyst (0.5% or 1.0% with respect to oil) with methanol or ethanol, whereas the second step is conducted with either methanol or ethanol and NaOH (0.5%) or an alkali methoxide as a catalyst. The transesterification of acidpretreated CDO, which is washed with distilled water and dried with MgSO₄, catalyzed by alkali alkoxides gives methyl and ethyl esters in 90% and 79% yields, respectively, after 1.0 h [4]. However, higher esters yields were obtained from refined corn oil (96% and 88%, respectively). The NaOH-catalyzed transesterification of the acid-pretreated CDO model (pure corn oil and a technical grade linoleic acid (60%)) with 6% of FFAs, neutralized with NaOH, provided ester yields of greater than 85% in 1 h, but the separation of the two product phases was prevented by water and soap formation [5]. On the other hand, the one-step acid-catalyzed esterification of the CDO model with 6% FFAs was slow and resulted in less than 20% yield for 4 h, while the base catalyst in the one-step base-catalyzed transesterification was mostly consumed by FFA, leading to the very low conversion into esters after 1.5 h [5].

Velázquez [88] studied the transesterification of CDO having a high content of FFAs with methanol or ethanol using NaOH or NaOCH₃ at 60 °C. In the first step, the feedstock was either pretreated with silica powder to remove the impurities or esterified with alcohol and sulfuric acid. In the second step, the pretreated CDO was transesterified with alcohol in the presence of NaOCH₃ at 60 °C. In the case of the untreated CDO, NaOCH₃ was more effective than NaOH, especially when ethanol was used as a reactant. The use of CDO treated with silica and NaOCH₃ slightly enhanced the ester yield (84.1%) in the 145 min reaction with ethanol, compared to the reaction with the untreated CDO (83.6%). An overall ester yield of about 94% was achieved with the pre-esterified CDO and both alcohols although the reaction time was longer with ethanol (1.5 h) than with methanol (1 h).

5.3. Comparison of various transesterification routes

Generally, the complete conversion of corn oils can be achieved by various transesterification methods. However, the presence of dimethyl ether as a co-solvent [87] or high temperatures, pressures, and alcoholto-oil molar ratios [101] were needed when homogeneously base- and acid-catalyzed processes were applied. Various research groups have applied different reaction conditions to heterogeneous catalysis to achieve high oil conversion, e.g., microwave irradiation and high temperature [99] or diethyl ether as a co-solvent and high alcohol-to-oil molar ratio [108]. Mata et al. [93] achieved biodiesel yield close to 99% by the use of absolute ethanol as a reactant, whereas Demirbas [97] used supercritical methanol at a high alcohol-to-oil molar ratio. Comparing biodiesel yields obtained in the base and enzymatic catalyzed routes, Mata et al. [93] demonstrated improved process performance when using enzymes, independently of the type and amount of alcohol. Moreover, Demirbas [97] concluded that supercritical process could compete with the base-catalyzed process because it reached the same biodiesel yield in about 25-times less time.

5.4. Comparison of the possible technologies for energy conversion from corn oil

As for other vegetable oils, energy conversion from corn oil can technically be conducted by transesterification and blending with other fuels (such as gasoline, naphtha, and ethanol). Other methodologies, such as direct use and the formation of microemulsions, have not been reported. On the other hand, bio-oil and bio-char can be produced from corn cobs and stover (stalks, leaves, and husks) by fast pyrolysis [116].

However, there have been no reports comparing the economic results of various biodiesel technologies that use the same or a variety of corn-oil-based feedstocks, and there is only one comparative economic analysis of the technology applied in biodiesel production from various oily feedstocks including refined corn oil [117]. Table 2 shows the comparison of the optimal reaction conditions and the efficacy of corn oil transesterification reactions. The economic viability of biodiesel production is mainly influenced by the price of the oily feedstocks, the production and equipment costs, the plant capacity, and the price of biodiesel, where the first-mentioned influential factor is the principal obstacle to the biodiesel market feasibility. Approximately 70-95% of the total biodiesel production cost depends on the cost of the raw material [1]. Accordingly, biodiesel price ranges from 0.2 US \$/L for waste and non-edible oils to over 2 US \$/L for palm and sunflower oils. Alptekin et al. [117] reported biodiesel cost of 1.62, 1.40 and 1.13 €/L for KOH-catalyzed methanolysis from corn oil, chicken fat and fleshing oil, respectively in a pilot plant (10 t). The production cost of corn oil biodiesel was higher than the cost of the other two biodiesels because of its higher price (about 3.5 times). On the other hand, the corn oil ester yield was slightly larger than the yields from the animal feedstocks, although the fuel properties of the produced methyl esters were close to each other and all met the ASTM biodiesel standard.

Another possible way of using corn oil as a fuel for diesel engines is

in the form of blends with petrol-diesel. This approach reduces the toxic emissions of the exhaust gases [118]. The optimal corn oil content in the blend is 10%. Both fresh and used corn oils have been blended with diesel and jet fuel mixed with butanol and ethanol [119]. The tested corn oil blends exhibit better combustion performance than fresh corn oil blends partly because of the higher unsaturation levels in fresh corn oil. Furthermore, these blending ratios of up to 30% exhibit similar cloud and pour points to those of petrol/diesel [120].

Because of its acceptable price (0.60 US \$/kg), the usage of CDO, taken from a local ethanol plant as biofuel feedstock for farming operations, has recently emerged [121]. CDO is blended with another less viscous fuel (other than petrol-diesel) such as gasoline, anhydrous or 99% purity ethanol, and naphtha. A modern agricultural diesel engine is compatible with these blends without any modifications, and blend ratios of 75/25 and 65/35 have been shown to perform better in some categories compared to the 85/15 blend.

6. Optimization and kinetics of biodiesel production from corn oil-based feedstocks

Statistical modeling and optimization methods have been widely used in recent years for the improvement of biodiesel production from neat and WFCO or the synthesis of CaO-loaded catalysts. For the homogeneous base-catalyzed transesterification of corn oil, ethanol-tooil molar ratio, catalyst concentration, and temperature are the main process factors affecting the conversion [90,94]. KOH is a better catalyst than NaOH in biodiesel production compared to refined corn oil and ethanol [95]. The statistical significance of the reaction variables affecting ester yield in the transesterification of corn oil with methanol catalyzed by an ionic liquid, decreased in the following order: MOMR > catalyst (ionic liquid) concentration > ultrasound power > reaction time > reaction temperature, but only the first three factors have a statistically significant effect [98]. For the transesterification of corn oil with methanol over Ba(OH)₂ in the presence of dimethyl ether as a co-solvent, the MOMR and the catalyst amount are statistically important at the 95% confidence level, whereas the effect of reaction time on conversion is insignificant [108]. Among the analyzed process factors, the agitation speed has little effect on the ester yield in the transesterification of WFCO over a CaO-based catalyst obtained from snail shells [107]. The optimal reaction conditions ensured an ester yield of 96%, in agreement with the predicted yield (96.8%). A significant cross-effect of the reaction time, DMC-to-oil molar ratio, and catalyst amount with respect to ester yield in corn oil transesterification with DMC over solid KOH is indicated by the elliptical shape of the response surface [103]. Continuous biodiesel production from corn oil has been statistically modeled and optimized by Ciftci and Temelli [129], who conducted this process in an SC-CO₂ bioreactor filled with immobilized lipase. According to the developed model, the ester purity depends on the MOMR, temperature, pressure and CO2 flow rate, although only the first two process factors have a positive effect. Moradi et al. [104,105] optimized the preparation of CaO-supported catalysts by the sol-gel method. For the CaO/SiO₂ catalyst, the calcination temperature and acid-to-water ratio were estimated [104], whereas for the CaO/y-Al₂O₃ catalyst, the gelation temperature and nitric acid concentration were analyzed [105]. All three process factors significantly influenced the ester purity and the yield obtained over the CaO/SiO₂ catalyst, but only the effect of the catalyst amount was positive.

The kinetics of transesterification reactions for biodiesel production from corn oil feedstocks has rarely been studied. An overview of the studies of the reaction mechanism and kinetics is given in Table 3. Although the researchers are aware of a complex reaction mechanism that includes three consecutive, reversible reactions, some of them use the simplified pseudo first- or second-order reaction rate law independently of the type of catalyst. The values of the activation energy for the conversion of TAGs into diacylglycerols (DAGs) are in the range of 47–90 kJ/mol, depending on the type of catalyst and alcohol and the

A review on the reaction	on mechanism aı	nd kinetic mode	els for tran	sesterification of corn oil.							
Type of reaction	Catalyst	Acyl acceptor	T, °C	Reaction mechanism	Kinetic model	Forward reaction r	ate constants, L/(m	ol min)		$E_{\rm a}$ kJ/	Reference
						TAG	DAG	MAG	TAG DAG	MAG	
Homogeneous base	NaOH	Methanol	45-70	Three consecutive reactions; irreversible	Pseudo-second-order	$0.031 - 0.18^{a}$	3.1-14 ^a	9.1–19 ^a	62.8 58.2	28.0	[88]
catalysis		Ethanol		with respect to TAG and reversible with respect to DAG and MAG	with respect to TAG, DAG and MAG	0.0053-0.025 ^a	2.6–12.7 ^a	3.1-14 ^a	66.5 68.6	30.5	
Homogeneous acid catalysis	H_2SO_4	Ethanol	155–195	Three consecutive reversible reactions	First order with respect to each reactant	0.00094-0.00396	0.00325-0.0115	0.00266-0.00708	47.4 55.8	46.0	[101]
Heterogeneous base catalysis	CaO/SiO ₂	Methanol	50-65	Irreversible overall reaction	Pseudo-first order with respect to TAG	0.1298–0.2954 ^b			49.9		[104]
	KOH, solid	Dimethyl carbonate	65–75	Irreversible overall reaction	Pseudo-second-order with respect to TAG and	0.0061-0.0143			83.3 89.8		[103]
Enzymatic catalysis under SC-CO ₂	Novozym 435	Methanol	4060	Irreversible overall reaction	Production order Pseudo-second order with respect to TAG	0.14-0.74			72.9		[110]
a (0% molor min) -1											

тім п.

Table 3

lowest value is observed for homogeneous acid-catalyzed transesterification.

For homogeneous NaOH-catalyzed transesterification of corn oil with methanol or ethanol, the pseudo second-order reaction rate with respect to TAGs, DAGs, and monoacylglycerols (MAGs) has been used by Velázquez [88] because of the excess of methanol in the reaction mixture. In the range 45-70 °C, the reaction rate constants for TAGs, DAGs, and MAGs increase with increasing temperature for both the alcohols, but their values are smaller for ethanol. Moreover, the kinetic constant for TAGs is one order of magnitude smaller than that when using ethanol, indicating that the reaction of TAGs with methanol is much faster than that with ethanol. The values of the activation energies for TAGs. DAGs and MAGs using methanol and ethanol are very similar (Table 3). In addition, the reported values of the activation energies (28-68.6 kJ/mol) for the three forward conversions of corn oil by homogeneously catalyzed transesterification are close to the values reported for the methanolysis of palm oil using KOH (26.8-61.5 kJ/ mol) [122], soybean oil using NaOH (21.7-83.1 kJ/mol) [123], and sunflower oil using KOH (33.2-53.5 kJ/mol, [124]). Furthermore, they are similar to the values reported for sunflower oil ethanolysis with NaOH as a catalyst (3.4-43.9 kJ/mol) [125]. The activation energy of the methanolysis reaction of acid-pretreated waste cooking oil, which is considered to be, overall, an irreversible first-order reaction, is reported to be 88.7 kJ/mol [126].

For the transesterification of corn oil catalyzed by trace sulfuric acid, Liu et al. [101] developed a complex kinetic model assuming no mass transfer limitation in the initial stage, no other compound in the corn oil except for TAGs and first-order reactions of the three-step reversible reactions with respect to each reactant. All forward reaction rate constants are proportional to the acid concentration and vary with temperature in accordance with the Arrhenius equation. The rate constant of the TAG conversion into DAG and alkyl esters is the lowest, confirming this step as the rate-controlling step in the overall reaction. Furthermore, the first two reactions are irreversible, while the third reaction is reversible.

The kinetics of corn oil transesterification over solid base catalysts has been investigated in two studies. Moradi et al. [104] assumed that corn oil methanolysis over a CaO/SiO2 catalyst occurs in one step as a pseudo-first-order reaction with respect to the TAGs. The apparent reaction rate constant increases with increasing temperature according to the Arrhenius equation with an activation energy of 49.9 kJ/mol [103]. For corn oil transesterification with DMC over solid KOH, Sun et al. [103] considered only the forward reactions for TAGs and DAGs and assumed the pseudo-second order with respect to the TAGs in the initial reaction stage. The activation energy of 83.3 kJ/mol agrees closely with the activation energy (about 79 kJ/mol) for palm oil transesterification with DMC over solid KOH [127] and waste cooking oil methanolysis using calcined snail shells [128] but is larger than the activation energy for the methanolysis of waste cooking oil (35.51 kJ/mol), sunflower oil methanolysis (32.2 kJ/mol), and canola oil (20.9-23.4 kJ/mol) over FeCl3-modified resin [129], solid Ba(OH)2 [113], and alumina-supported potassium [130], respectively.

Assuming that the reaction is irreversible, Ciftci and Temelli [110] determined enzymatic biodiesel synthesis in a batch $SC-CO_2$ bioreactor with a low excess of methanol to be pseudo-second-order. The activation energy of 72.9 kJ/mol is higher than that for chemically catalyzed transesterification with methanol and lipase-catalyzed transesterification of some waste oils such as baked duck oil [131] and cooking oil [132] in the presence of combined lipases (Novozym 435 and Lipozyme TLIM) with no co-solvent or with *tert*-butanol, which were 31.7 and 51.7 kJ/mol, respectively.

7. The possibilities for improvement of corn-based biodiesel production

Biodiesel production from corn oil-based feedstocks can be

improved by simplifying the process, enhancing the ester yield and shortening the reaction time. In recent years, several different methods, such as the application of in situ transesterification, ultrasonic energy, microwave irradiation, ionic liquids, co-solvents, supercritical conditions and the integration of reaction and separation processes have emerged, aiming at improving the transesterification of corn-based feedstocks. The integration of ethanol and biodiesel production from corn could also result in techno-economic improvement in the overall production process.

After separating the germ from the endosperm in the whole corn kernel processing stage, the resultant germ can be subjected to in situ transesterification. Shi et al. [78] compared three possible routes for ethanol and biodiesel production from six new Korean corn varieties: a) whole corn kernel milling, fermentation, and in situ transesterification; b) whole corn kernel milling, in situ transesterification, and fermentation; and c) the separation of germ and endosperm from whole corn kernels, in situ transesterification of the germ, and fermentation of the endosperm and transesterification residue. The high biodiesel yield of the third route is due to the use of oilrich germ and the lack of an effect of the endosperm on in situ transesterification. A slightly lower biodiesel yields in the second route was explained by the negative effect of endosperm on the contact between the germ or oil and the solvent and catalyst during the transesterification process. The one-step in-situ process provided a higher esters yield compared to the traditional twostep method because it did not rely on oil extraction.

Positive effects of ultrasonic and microwave irradiation have also been observed for the transesterification of corn oil in a few studies (Table 2). Fernandes et al. [94] achieved esters yield of about 63% for only 30 min in the low-frequency high-intensity ultrasound-assisted transesterification of corn oil with ethanol at 28 °C and atmospheric pressure. This ethyl ester yield is lower than that (93.1%) obtained by corn oil methanolysis under somewhat different reaction conditions [133]. The positive effects of increasing the reaction temperature, stirring rate and ultrasonic irradiation power on methyl ester content in the transesterification of corn oil with methanol have been demonstrated by Lee et al. [91]. Compared to the conventional heating method, ultrasonic biodiesel production reduced the reaction time by about 30 min and increased the oil conversion degree. For the corn oil transesterification reaction performed at an ultrasonic power input of 450 W, the ultrasonic energy density of 4926.5 kJ/L is lower than those of canola and soybean oils [91].

Further improvement of biodiesel synthesis may be achieved by combining unconventional heating methods with novel ionic liquid catalysts [134]. Bi and Wu [98] confirmed the significant effect of the ultrasonic power on biodiesel production in the presence of an ionic liquid catalyst. On the other hand, using different diphenylammonium salts (tosylate, benzenesulfonate and mesylate) as ionic catalysts in the same transesterification reaction at a high temperature, Majewski et al. [99] drastically increased the reaction rate and achieved the complete conversion in a seven-times shorter reaction time compared to the traditional heating method.

Dimethyl ether, diethyl ether, and tetrahydrofuran are commonly used as co-solvents in biodiesel production from corn oil. In the presence of diethyl ether and $Ba(OH)_2$ as a catalyst, a high biodiesel yield of 99.15% was obtained under the optimum operating conditions for 2 h [108]. With tetrahydrofuran or dimethyl ether, a complete conversion of corn oil in the presence of KOH (0.5%) was reached in only 20 min at room temperature [87]. Moreover, with dimethyl ether, complete conversion was achieved in less than 20 s at a KOH concentration of 1%.

Integration of the reaction and separation processes in a single stage using a continuous membrane reactor is another way to improve the economics of biodiesel production processes. This technology was utilized for NaOH-catalyzed biodiesel production from pre-treated and refined corn oils at 65 °C [92]. The residence time influenced the pressure inside the reactor but not the produced biodiesel quality. For



Fig. 6. Integrated production of ethanol and biodiesel from corn.

the refined corn oil, the critical flux was greater than $70 \text{ L/(m}^2 \text{ h})$, whereas half the flux was needed for the pre-treated corn oil to stay within the pressure limitation of the membrane reactor.

Another possibility for the improvement of corn-based biodiesel production is its integration into existing ethanol production plants [4,135]. Ethanol and corn oil, a primary product and a by-product from corn ethanol plants, respectively, can be utilized as feedstocks for the biodiesel plant operating within the same general facility (Fig. 6). Currently, many existing ethanol plants already recover corn oil from DDGS and convert it to biodiesel. The set -up of corn oil recovery equipment facilitates the production of corn oil as feedstock for biodiesel production without affecting the existing ethanol production. Furthermore, the addition of a 'bolt-on biodiesel' plant to existing ethanol plant results in significant capital savings and ongoing production cost efficiencies over conventional biodiesel processes. Among the many competitive advantages of the integrated ethanol/biodiesel production are the reduced transportation and procurement costs, shared infrastructure, and the ability to merge the co-product streams resulting in multiple revenue possibilities. Furthermore, DDGS-corn oil ethanolysis results in a truly bio-derived fuel as a petrol/diesel alternative. The benefits from these emerging integrated biorefineries will drive the improvement of existing technologies (both in oil recovery and biodiesel synthesis stages) and increase biodiesel competitiveness with petrol-diesel, resulting in further expansion of corn-based biodiesel production.

8. Fuel properties of corn-based biodiesels

The most important physicochemical and fuel properties of cornbased biodiesels reported in the literature are presented in Table 4. Generally, most of the properties meet the biodiesel quality standards, with a few exceptions [93,103,114]. For the biodiesels obtained by the base and enzyme-catalyzed transesterification of corn oil with absolute methanol and ethanol, the viscosity, water content, acid value and group I metals are outside the EN 14214 standard limits [93]. Ethanolic biodiesel has higher viscosity and water content than methanolic biodiesel. The water content is significantly greater than the standard limit. The value of alkaline metals above the maximum limit for both alcohols increases the possibility of the metallic soap and abrasive solid formation and may block the filters and injectors in the engine. The kinematic viscosity of biodiesel obtained by Sun et al. [103] is out of the range of the EN 14214 standard limit, but it corresponds to the ASTM D6751 standard. In addition, the kinematic viscosity and an acid value of DDGS lipid-based biodiesel do not meet the biodiesel specifications because the conversion is not completed [114].

9. Environmental, socio-economic and policy aspects of biodiesel production from corn

There has been almost no investigation of the environmental, socioeconomic and policy implications of biodiesel production from corn oil. However, they have been thoroughly analyzed for corn cultivation, corn oil production, and corn-based ethanol production [12,138,139], and can be partly involved in the assessment of corn-oil-based biodiesel production. Besides that, many studies on the production and use of biodiesel from other feedstocks have been carried out with the purpose of evaluating these implications [1]. One can expect that the implications of corn oil-based biodiesel are the same or similar to those linked to the biodiesel produced from other food crops. First, the use of corn oil as a renewable resource will mitigate climate change because the dominant greenhouse gas, CO₂, is consumed by plants during photosynthesis. In addition, the increased biodiesel production from corn oil will not only reduce CO₂ emissions but also reduce the negative impacts on air, water, land and biodiversity, as well as promote agricultural growth and rural economic development. Second, the use of corn oil as fuel will bring up the food versus fuel controversy because corn oil is being converted into biofuel while famine is widespread in the world. In addition, because corn grain is traded on the international markets. an increase in biofuel production globally will result in a rise in energy and corn prices. Until now, only Wang et al. [140] pointed to the careful co-product treatment approach when estimating the greenhouse gas emissions within the life-cycle of corn oil biodiesel. The intensities of these emissions from the three methods developed for the treatment of the co-products (marginal, hybrid allocation and process-level energy allocation) are 14, 59, and 45 g CO₂e/MJ, respectively. With the fourth method, named displacement, corn oil biodiesel is burden-free. A sensitivity analysis shows that the greatest influence of corn oil recovery energy consumption on biodiesel production is related to the marginal approach, and no parameter has an influence greater than 4% within the hybrid and process-level emissions. Third, because corn is grown as a food crop with modern, large-scale, mechanized, high-input agricultural methods, several environmental problems will arise because of the reliance on pesticides, fertilizer use (pollution of waterways) and high energy consumption. Fourth, the growth of biodiesel production from corn oil may contribute to energy security and is intimately connected with agricultural production. All these economic, environmental and social impacts are generated at all stages of corn cultivation and processing and biodiesel production, but the processes connected to land-use change and intensification are dominant [141]. Taheripour and Tyner [11] employed a model (the so-called GTAP-BIO model) for estimating the induced land-use emissions arising from ethanol and biodiesel production using new technology and confirmed the expectation that corn oil extraction would reduce the induced landuse emissions arising from total biofuel production. They also showed that the allocation method selected for corn oil could have a significant impact on the estimated land-use change emissions.

10. Conclusion

The potential of corn for this application lies primarily in the oilcontaining co-products of industrial corn processing, such as corn germ

Table 4 Properties of corn-based 1	biodies	el.																				
Property, unit	CME ^a	CME ^b	CME ^c	CME ^d	CEE ^e	CEE ^f	CEE	CME	CME ⁸	CME ^h	CME	CME ⁱ	CME ^j	CME I	OGME	CME and ULSD blend (B20)	DGME and ULSD blend (B20)	CEE and ULSD blend (B20)	DGEE and ULSD blend (B20)	CME	CME	EN14214 limit, min/ max
FAME content,% Density at 15°C ko/m ³	865	871	895	882	879	890	875.1		890 ^k	886.4	882 k	877.1	877.9	887 8	12	85.6	856	854	854	875 ^k	860	96.5 min 860/900
Viscosity at 40 °C, mm ² /s	4.14	4.72	5.82	4.71	6.56	9.15	4.6		2.4	4.83	4.06	4.095	4.005	5.9	24	2.52	2.48	2.52	2.60	4.22 ¹	4.52	3.50/5.00
Flash point, °C				150	150	150	180			168		169	171	212						143	165	101 min
Sulfur content, mg/kg Carbon residue (on 10%													J	0.03		9	9	9	9			10 max 0.30 max
distillation residue),%																						
Cetane number Sulfared ash content %							51.5			43				49 0.01								51 min 0.02 max
Water content, mg/kg Total contamination mg/	150	210	290	935	1653	1966	470.2			433	300					57	57	62	61			500 max 24 may
kg																						V0111 - 7
Copper strip corrosion (3 h				1	1	1								2								Class 1 min
at 50 CJ, tatung Oxidation stability at							7.75									6.9	5.0	9.6	5.4			6.0 min
110°C (h)		10 0					L C				0			0 L	00			0				
Acid value, mg KOH/g Iodine value. g I ₂ /100 g	0.047 126.6	0.21 98.4	 80	0.36 123.7	1.49 118	0.6 92	c.0		0.4	1.34 102	0.3 123		-	5 29.0	.87	0.13	0.13	0.13	0.16			0.50 max 120 max
Polyunsaturated $(\geq 4$																						1
double bonds) metnyi esters.%																						
Methanol content,%																						0.20 max
Monoglyceride content,%	0.4	0.27	0.3					0.235 - 0.243														0.80 max
Diglyceride content,%	0.11	0.1	0.1					0.029-0.039														0.20 max
Inglycende content,%	500	500	50.0				000	0.003-0.013														0.20 max
Free glycerol.% Total glycerol.%	10.0	10.01	10.0				0.19	0.003-0.007					0	0.13								0.25 max
Group I metals (Na+K),				13.5	11.8	11.8																5.0 max
mg/kg Group II metals (Ca + Mo)																						5 0 may
mg/kg																						VIIII 0.0
Phosphorus content, mg/														0.2								4.0 max
kg Cold filter plugging point, °د	8	8	6-	-7.3	+	+						-2	- 4									-5 max
ح Peroxide value. mea/Kø	3.0	14	31.8																			Not specified
Cloud point, °C	ا د	4	ε Γ							0				-2	-8.48	-12.1	- 12.2	-13.3	-12.7			Not specified
Pour point, °C	9-	9-	- 5						- 11	-3		00.00	20 DE	-16 25.4 3	69 0	- 19.7 44 4	- 18.0	-20	-18 44 20	93 67	00 00	Not specified
rugner neaung value, MJ/ kg										40.01		06.60	66.60	4.00	C0.2	1 .	4.4	44.12	44.20	00.24	70.00	NOL Specified
Distillation range,°C																						Not specified
																				U	continu	ed on next page)

EN14214 limit, min/ max		
CME	[137]	
CME	[136]	
DGEE and ULSD blend (B20)		
CEE and ULSD blend (B20)		
DGME and ULSD blend (B20)		
 ² CME DGME CME and ULSD blend (B20) 	[89] [114] [4]	
E ⁱ CMI	_	
E CMI	8] [96	
E ^h CM	7] [10	
E ⁸ CM	3] [10	
CIM	[10	
CME	[92])	
CEE	[95]	
CEE ^f		
CEE		
CME ^d	[63]	
CME		
CME ^b		
CME ^a	[06]	
Property, unit	Reference	

CEE - corn oil ethyl ester. DGEE - distillers grains ethyl ester. ULSD - ultra-low sulfur diesel fuel. DME - corn oil methyl ester. DGME - distillers grains methyl ester.

Before storage of biodiesel.

Fable 4 (continued)

- After storage under argon atmosphere.
- After storage under normal oxygen atmosphere.
- Alkali-catalyzed process with absolute methanol
 - Alkali-catalyzed process with absolute ethanol.
- Enzyme-catalyzed process with absolute ethanol
- heterogeneous process with dimethyl carbonate as an acyl acceptor.
 - WFCO as feedstock
- NaOH as catalyst.
 - KOH as catalyst
 - At 20 °C. At 30 °C.

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and DDGS or CDS from starch and ethanol production. Nowadays, many ethanol-producing companies are developing technologies for the separation of corn germ prior to ethanol fermentation or the recovery of the residual corn oil from corn germs or DDGS and its conversion into biodiesel. Simpler, more effective and energy-saving technologies for biodiesel production should be developed, which will include cheaper, more efficient and reusable solid catalysts, continuous reactors with improved mass transfer characteristics, and the integration of reaction and separation phases in a single stage. Furthermore, ethanol and biodiesel production should be integrated into the biorefinery concept, which will result in the production of many other high value added products with near-zero waste.

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