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A summary of the available technologies for biodiesel production based on a comparison of different feedstock's properties

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ABSTRACT

Biodiesel production is mainly done by carrying on the transesterification reaction while using refined oil, methanol and a homogeneous base catalyst. When using refined oil, a competition between oil for food and oil for fuel is then presented. Even more, the conventional technology has the disadvantage that the raw material has to be very pure, with no traces of other impurities. Otherwise, undesirable products will be produced decreasing the productivity of the process and making a large amount of waste treatment.

Because of this, other technologies appear as possible sources for biodiesel production, mainly from refined oil, but also allowing less pure raw material to be used, such as waste oil, frying oil, soapstocks, and animal fats.

In this work, a comparison of all these different raw materials, their physicochemical properties and how they can have an influence, and the magnitude of this phenomenon, in the biodiesel production will be presented and compared. Based on the previous analysis, a short summary of the technological possibilities to produce good quality biodiesel from low price raw material will be discussed with the aim of showing their advantages and disadvantages when using different feedstocks.

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Keywords: Biodiesel production; Edible and non-edible oils; Technological process

1. Introduction

Biodiesel is defined as the monoalkyl ester of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats. The main reaction to produce this fuel is the transesterification reaction, where triglyceride interacts with an alcohol to produce ester and glycerol (the reaction is seen in Scheme 1). This alternative fuel has several environmental advantages, such as less CO₂ emissions, almost zero CO and sulfur emissions, it is biodegradable and it has a better lubricity effects for the engines due to vegetable oil origin, and therefore, it prolongs the engines life. However, it has some drawbacks; for example, it requires additives if used in cold weather (Marchetti et al., 2007; Srivastava and Prasad, 2000; Ma and Hanna, 1999; Fukuda et al., 2001; Knothe et al., 2005).

Normally, biodiesel is produced by a transesterification reaction of refined oil in the presence of methanol and using sodium hydroxide as catalyst. This technology is well established and several works could be found addressing several points of this technology (Marchetti et al., 2007; Srivastava and Prasad, 2000; Ma and Hanna, 1999; Fukuda et al., 2001; Knothe et al., 2005; Schuchardt et al., 1998; Noureddini and Zhu, 1997; Freedman et al., 1984; Vicente et al., 2004; Alamu et al., 2007). The biggest drawback of this process is the need of refined oil, meaning that the amount of impurities are extremely low; for example, the amount of free fatty acids (FFA) must be lower than 0.5% (Marchetti et al., 2007; Srivastava and Prasad, 2000; Fukuda et al., 2001; Barnwal and Sharma, 2005). This has produced a great debate between oil for food vs. oil for fuel, since the refined oil is the oil required for feed purposes.

In order to use less pure raw material, such as frying oil, soapstocks, and waste oil, different technological solutions have been proposed. It could be found that an option that uses homogeneous acid catalyst, normally sulfuric acid (Zheng

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		2		
$C\Pi - OOC - K_2 + SK$	Un ↔	K2-COO-K	T	00-00
CH_2 -OOC- R_1	Catalyst	R ₁ -COO-R'	+	CH ₂ -OH

Scheme 1 - Transesterification reaction.

et al., 2006; Canakci and Van Gerpen, 2003a,b; Van Gerpen, 2005); this will allow the process to carry on the esterification reaction of FFA simultaneously with the transesterification of triglycerides. However, the transesterification reaction is 4000 times slower compared when Na(OH) is used as catalyst; and therefore, it is generally used as a pre-esterification step (Marchetti et al., 2008).

Other alternatives include the use of heterogeneous catalyst, such as solid resin and immobilized enzymes. It has been proved that heterogeneous catalysts have a great potential, not only from a technological point of view, but also from an economic approach (Marchetti et al., 2008; Marchetti and Errazu, 2008a). Technically, it has been presented that they are suitable to carry on the esterification as well as the transesterification reaction simultaneously achieving good conversions (Bournay et al., 2005; Chakrabarti and Sharma, 1993; Gangadwala et al., 2006). It has also been shown that this technology has a promising scope from an economic point of view. On the other hand, enzymes seems to be the most environmental friendly alternative, showing that the operational conditions are less drastic than those required for other technologies due to the live nature of the catalyst. Several works, such as those from Bajaj et al. (2010), Ranganathan et al. (2008) and Antczak et al. (2009), among others, have shown that the use of enzyme could give high conversion in the range of over 90% (Bajaj et al., 2010), 94.8% (Antczak et al., 2009) and 98.5% (Antczak et al., 2009), to show some results. However, its price is the major drawback. Monolithic reactors, membrane reactors or super critical alternatives are other options that are suitable to produce biodiesel of high quality and giving high final conversion (Tonetto and Marchetti, 2010).

Based on the different technologies and the different possible raw materials (qualities of vegetable oils and animal fats), this work intends to point out the advantages and disadvantages of several technologies based on the quality of raw material that they are normally capable of treat to produce biodiesel.

2. Types of vegetable oils

Biodiesel is normally generated from refined oil, which is defined based on the amount of impurities. In this case, the oil has been degummed, with no phospholipids, tocopherols, water, and free fatty acid among other impurities that might be presented depending on the origin of the oil. If the oil is a frying waste, it might have traces of particulate matter due to cooked food.

This pure raw material is most commonly used due to the type of catalyst employed on a typical biodiesel production plant. If the oil has impurities, such as free fatty acids, the basic homogeneous catalyst will be consumed due to a soap

 $\text{R-COOH} \quad + \quad \text{Na(OH)} \quad \rightarrow \quad \text{R-COONa} \quad + \quad \text{H}_2\text{O}$

Scheme 2 – Soap formation reaction.

formation reaction (see Scheme 2), instead of taking part on the transesterification reaction that will lead to the biofuel.

In order to properly compare the different types of raw material, it is important to see the major properties of each type of oil. Table 1 shows a comparison between refined, crude and waste oil for 8 main properties.

From Table 1 it is seen that as much impurities the oil has the higher is the viscosity, this could be due to the different impurities as well as traces of particulate matter in the waste oil. On the other hand, the cetane number is quite close for refined as well as crude oil. When comparing the impurities, such as acid value and sulfur content, most impurities appear for the waste oil, which is expected. In the case of sulfur content, the waste oil has a percentage that is over 350 times higher than the one presented in the refined oil.

The amounts of impurities on the waste, frying, soapstocks oil are generally quite high, requiring purification (as presented in Table 1). There is another source of oil called nonedible oils where their purity is not as relevant as for the edible oils since they could not be use for feed purposes.

Based on the fact that non-edible oils are also a new source of raw material, but not necessarily a waste, a comparison between non-edible and edible oils properties is important to be presented (Chhetri et al., 2008). This is seen in Table 2.

Even more, it is important to see the chemical composition of the different oils, mainly the edibles and non-edibles, since the final biodiesel will have different fuel properties depending on the raw material (Gui et al., 2008). Table 3 shows the composition (chain length and number of double bonds) for some of the most common vegetable oils used as raw materials.

Different vegetable oils grow in different areas of the world due to climate conditions as well as soil properties. O'Brien et al. (2000) have done a very descriptive work where it pointed out the productive areas. Table 4 shows the landscape areas for several different seeds and an estimation of how much oil could be produce from each type of seed.

3. New source for oil

Due to the ongoing debate of fuel vs. food, different non-edible oils have been used for biodiesel production. However, the search for new sources have not stopped and a new alternative have appeared over the last years, oil from micro and macroalgae.

Algae are very simple organisms that are aquatic and in the microscopic scale. They can be used for different types of fuels, such as: biodiesel from microalgae oil, photo biologically produced of bio-hydrogen and methane production from anaerobic digestion (Spolaore et al., 2006; Ghirardi et al., 2000; Dunahay et al., 1996). The use of microalgae for biofuel has several advantages (Mata et al., 2010):

- $\bullet\,$ Algae required CO_2 to grow and therefore it will consume this pollutant from industrial gases and combustion engines.
- Algae could easily grow in water that is not suitable for human consumption; therefore there will be no conflict with drinking water supplies.
- Algae could be easily produced in areas where no other agricultural seed might grow.
- Several other chemical compounds could be produced from algae as feedstocks.

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Table 1 – Properties of the major types of oil.								
Property	Refine (Chhetri et al., 2008; Demirbas, 2008)	Crude (Jathropa based) (Singh and Padhli, 2009)	Waste (Zhang et al., 2003; Dmytryshyn et al., 2004; Phan and Phan, 2008; Anastopoulos et al., 2009)					
Kinematics viscosity [mm²/s]	30.2	35.4	40.2					
Carbon residue [wt%.]	0.24	0.3	0.18					
Cetane number	38.01	23	-					
Higher heating value [MJ/kg]	39.41	33	24.67					
Ash content [wt%]	0.012	0.7	-					
Sulfur content [wt%]	0.013	0.02	5					
Iodine value [centigram I/g oil]	112.86	101	13.2					
Acid value [mg KOH/g oil]	<0.2	11	5.96					

Table 2 – Properties of biodiesel from different sources.

Parameters		No	n-edible oils		Edible oils		
	Jatropha	Rubber	Castor	Pongamia pinnata	Soybean	Palm	Rapeseed
Viscosity	4.8	5.81	-	4.8	4.50	4.42	4.08
Specific gravity	-	0.874	0.960	-	0.882	0.86	0.885
Calorific value [MJ/kg]	39.23	36.50	39.5	-	37.00	-	39.76
Flash point [°C]	135	130	260	150	170	182	69
Cloud point [°C]	-	4	-12	-	-4	15	-2
Pour point [°C]	2	-	-32	-	-12	15	-3
Ash content [wt%]	0.012	-	0.020	0.0005	-	0.020	-
Acid value [mg KOH/g]	0.400	0.118	-	0.620	-	0.080	-

Source: Extracted from reference Gui et al. (2008).

Table 3 – Vegetable oils composition.

Vegetable oil	Fatty acid composition [% by weight]								
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00

Source: Extracted from reference O'Brien et al. (2000).

Table 4 - Major producer for several vegetable oils.

Seed	Amount of oil [%]	Productive areas
Canola	40–45	Canada, China, India, France, Austria, United Kingdom, Germany, Poland, Denmark, Check Republic.
Corn	3.1–5.7	USA, Mexico, Russia, Belgium, France, Italy, Germany, Spain, United Kingdom.
Cotton	18–20	China, Russia, USA, India, Pakistan, Brazil, Egypt, Turkey.
Peanut	45–50	China, India, Nigeria, USA, Senegal, South Africa, Argentina
Crocus	30–35	China, USA, Spain, Portugal
Soybean	18–20	USA, Brazil, Argentina, China, India, Paraguay, Bolivia
Sunflower	35–45	Russia, Argentina, Austria, France, Italia, Germany, Spain, United Kingdom.
Coconut	65–68	Filipinas, Indonesia, India, México Sri Lanka, Thailand, Malaysia, Vietnam, Mozambique, New Guinea, Republic of Côte d'Ivoire
Olive	15–35	Spain, Italy, Italia, Greece, Tunes, Turkey, Morocco, Portugal, Syria, Algeria, Yugoslavia, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, USA, Australia.
Palm	45–50	Malaysia, Indonesia, China, Filipinas, Pakistan, México, Bangladesh, Colombia, Nigeria, Republic of Côte d'Ivoire
Palm kernel	44–53	Malaysia, Indonesia, China, Filipinas, Pakistan, México, Bangladesh, Colombia, Nigeria, Republic of Côte d'Ivoire

Source: Extracted from reference O'Brien et al. (2000).

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Table 5 – Oil content for several microalgae (Chisti, 2007).						
Microalgae	Oil content [% dry wt.]					
Botryococcus braunii	25–75					
Chlorella sp.	28–32					
Crypthecodinium cohnii	20					
Cylindrotheca sp.	16–37					
Dunaliella primolecta	23					
Isochrysis sp.	25–33					
Monallanthus salina	>20					
Nannochloris sp.	20–35					
Nannochloropsis sp.	31–68					
Neochloris oleoabundans	35–54					
Nitzschia sp.	45-47					
Phaeodactylum tricornutum	20–30					
Schizochytrium sp.	50–77					
Tetraselmis sueica	15–23					

Table 6 – Oil content for several microalgae (Mata et al., 2010).

Plant source	Biodiesel productivity [kg biodiesel/ha year]
Corn	152
Hemp	321
Soybean	562
Jatropha	656
Camelia	809
Canola	862
Sunflower	946
Castor	1156
Palm oil	4747
Microalgae (low oil content)	51.927
Microalgae (medium oil content)	86.515
Microalgae (high oil content)	121.104

The main chemical composition of several algae was presented by Demirbas (2009), showing the main contribution of lipids, carbohydrates, proteins and nucleic acid. Nevertheless, if the conditions are favorable, algae could produce oil, this being oil content variable according to the source. Table 5 shows different types of microalgae and the oil content for each of them (Chisti, 2007).

Another important variable when considering the production of oil is the required landscape. In the case of algae, Chisti (2007) has found that the amount of oil produced for a determinate landscape area is at least one order of magnitude higher than for the best vegetable oil from crop, and in some cases it could be over 23 times bigger.

Due to the versatility of this new source of oil, it is important to see the productivity level. Mata et al. (2010) have done a comparison on the biodiesel productivity for several plant sources; this is reproduced in Table 6. From Table 6 it can be seen that the biodiesel productivity for the high oil content microalgae is 25 times bigger than the productivity when vegetable oil are used.

4. Properties of the fuel based on the raw material

All vegetable oils have different compositions, as shown in Table 3. This means that the biodiesel produce will be composed of different fatty acid chains. The different fatty acid compositions modify the biodiesel main properties, such as low temperature operability, oxidative and storage stability, kinematics viscosity, exhaust emissions, cetane number, and energy content (Moser, 2009).

Several properties for different types of biodiesel have been compared by Moser (2009). The author used different types of fatty acid, from C12 to C18 with one, two and three double bonds; it was also used in ethanol and butanol as well as methanol to carry on the reaction.

Table 7 presents this comparison. It can be seen that the biodiesel produced with ethanol has a lower melting point temperature when compared with methyl esters. Oil stability index is very low for large hydrocarbons chains, such as C18:3, being over 40 for C12 to C16. Regarding the cetane number, it is found that in almost all cases the cetane number is over the limit imposed by international standards (47 for ASTM D6751).

5. Production technologies comparison

As previously pointed out, biodiesel could be produced by several different technological possibilities, using homogeneous catalyst (acidic (Canakci and Van Gerpen, 2003a,b; Van Gerpen, 2005) and basic (Freedman et al., 1984; Vicente et al., 2004; Alamu et al., 2007)) as well as heterogeneous catalyst (solid

Table 7 – Properties of different biodiesels (Moser, 2009).								
FAEE	Melting point [°C]	∆ _c H [MJ/mol]	Kinematics viscosity [mm²/s]	Oil stability index [h]	Cetane number	Lub [µm]		
C12:0 ME	5	8.14	2.43	>40	67	416		
C12:0 EE	-2		2.63	>40				
C14:0 ME	19	10.67	3.30	>40		353		
C14:0 EE	12		3.52	>40				
C16:0 ME	31	10.67	4.38	>40	86	357		
C16:0 EE	19		4.57		93			
C16:1 ME	-34	10.55	3.67	2.1	51	246		
C16:1 EE	-37							
C18:0 ME	39	11.96	5.85	>40	101	322		
C18:0 EE	32		5.92	>40	97			
C18:0 BE	28		7.59		92			
C18:1 ME	-20	11.89	4.51	2.5	59	290		
C18:1 EE	-20		4.78	3.5	68			
C18:1 BE	-26		5.69		62	303		
C18:2 ME	-35	11.69	3.65	1.0	38	236		
C18:2 EE			4.25	1.1	40			
C18:3 ME	-52	11.51	3.14	0.2	23	183		
C18:3 EE			3.42	0.2	27			

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R-COOH + R_1 -CH₂OH \rightarrow R-COO-CH₂- R_1 + H₂O

Scheme 3 – Esterification reaction.

resin (Bournay et al., 2005; Chakrabarti and Sharma, 1993), enzymes (Ranganathan et al., 2008; Antczak et al., 2009)), but also with supercritical alcohol and with membrane reactor separation (Tan et al., 2011; Dubé et al., 2007).

All these technologies are capable of producing biodiesel from refined oil, which is the most common source of raw material for this fuel. However, not all of them are capable of generating the biofuel from a less pure raw material. In the case of basic homogeneous catalyst, the soap formation, as pointed out in Scheme 2, will consume the catalyst, reducing the catalytic properties of the process, not allowing the transesterification reaction to take place due to the lack of catalyst in the reaction medium. This is due to the speed of the soap formation reaction, this being one much faster than the esterification reaction. Even more, the triglycerides could be hydrolyzed in the presence of water, producing more free fatty acids that will consume more catalyst until it disappears. In order to avoid this, a pre-treatment process before the alkaline transesterification is needed (Nasirullah, 2005).

When using acid homogeneous catalyst, such as sulfuric acid, a more impure raw material could be used since this technology can treat free fatty acid and the presence of water. However, the transesterification reaction is 4000 times slower and, therefore, is less attractive for industrial purposes. On the other hand, due to the possibility of handling some more impurities, this option is normally used as a pre esterification step, allowing the conversion of free fatty acids into ester (Marchetti and Errazu, 2008b).

On the heterogeneous catalyst side, there are several options. Some solid resins are more suitable to carry on the transesterification reaction, reaching very good reaction rates as well as final conversion (Bournay et al., 2005). However, they are not always suitable for less pure raw materials. The main problem with some of these catalysts is their deactivation due to the presence of water, which is normally produced from the esterification reaction. Scheme 3 shows the esterification reaction.

Some other solid resin catalysts do not get deactivated due to the presence of water; however, the transesterification reaction takes place over an extremely high reaction time, making it unviable for an industrial process without optimization (Marchetti and Errazu, 2010). As with the acidic homogeneous catalyst, it is possible to use some of these solid catalysts as fixed bed reactors for the pre esterification step. Solid catalyst in both steps (pretreatment as well as main reaction) will give a more environmental friendly process due to the lack of separation, purification and washing required in comparison with homogeneous alternatives. Therefore, a combination of both processes with heterogeneous catalyst seems like a very interested possibility to produce biodiesel from very impure raw material as well as to have a much cleaner process.

Enzymes are a good possibility to produce biodiesel, they can easily treat fatty acid as well as triglycerides to produce biodiesel from non-edible or waste oil, reaching high conversion (Bajaj et al., 2010; Ranganathan et al., 2008). Although conversions are high, the reaction time it could be considered slightly high and therefore an optimization should be done in this technology as well. It is important to point out that this technology is the one with the less drastic operational conditions due to the live nature of the enzymes. However, the major drawback of this technology is the price of the catalyst, making it a non-viable economic technology to produce biodiesel (Bajaj et al., 2010).

A new approach has been done while using supercritical alcohols, supercritical methanol and ethanol (Warabi et al., 2004; Kusdiana and Saka, 2004; Tan et al., 2011). This technology has several advantages; it is extremely fast (less than 5 min to assure complete conversion), and is also suitable to treat almost any raw material with several impurities, among other benefits. The major drawback is the possible high cost related to high temperatures and pressure required to achieve the desirable operational conditions (Marchetti and Errazu, 2008a). Even though it might be more expensive than other technologies, the final product will be more pure, due to the lack of a catalyst. The separation process will be simpler, since the final product will have fewer components and there is no need for washing and neutralization, therefore it is a more environmental friendly process.

New technologies are being developed daily, such as membrane reactors for biodiesel production using conventional catalyst, showing good results and high final conversion and quite pure final product (Dubé et al., 2007). Other options are monolithic reactors, in this case the main problem is related

Table 8 – Comparison of different technologies for biodiesel production (Marchetti, 2009).								
Variable	Base	Enzyme	Supercritical	Monolithic	Resin	Acid		
Temp. [°C]	60–70	30–50	200–350	50–180	60–180	50-80		
Products from FFA	Soaps	Esters	Esters	Esters	Esters	Esters		
Effect of water ^a	\downarrow	\downarrow			\downarrow			
Yield to ester	Normal	High	High	Normal	Good	Normal		
Purification of glycerol	Difficult	Simple	Simple	Simple	Simple	Difficult		
Reaction time ^b	1–2 h	8–70 h	4–10 min	6 h	Variable	4–70 h		
Ester purification	Difficult	Simple	Simple	Simple	Simple	Difficult		
Cost	Cheapest	Expensive	Expensive	Medium	Medium	Cheaper		
Amount of equipment	High	Low	Low	Low	Low	High		

^a In this case the down arrow means that water is a draw back while the line means that is not effected and the system will be able to treat a raw material with some amount of water. For the enzyme case, a down arrow has been supply, in this case it is important to say that it is believed that some water is required for enzyme activation; however, a lot of water will produce a deactivation of the catalyst. In the case of the resin, it could be seen a down arrow as well as a line, this is due to the fact that water has different effects over different solid catalysts. In the case of the monolithic scenario, a line has been selected due to the fact that leaching is not caused by water per se but for a non-stability of the catalyst.

^b The reaction time set in this table is what it is most likely, however, it is important to point out that other times for the same technology could be found in the open literature.

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to the leaching of the catalyst from the heterogeneous to the homogeneous phase, changing the system to a homogeneous technology with the need of purification and separation of the catalyst after the reaction (Tonetto and Marchetti, 2010). New approaches for developing monolithic catalyst should be done in order to find a more stable choice that will not suffer leaching or will reduce this problem to a minimum. On the other hand, this technology could treat triglycerides as well as fatty acid and water does not seem to be a problem for the reactions involved, therefore it is a promising technology that should continue to be studied and developed.

In order to compare all these technologies based on some of the most important variables that should be considered, a resume over all the previous alternatives is seen in Table 8 (Marchetti, 2009).

In Table 8 it is seen that, except for the base technology, all the other are capable of producing ester from a less pure raw material with content of FFA. Also, water which affects some of the process does not have influence in other technologies, allowing these cases to produce biodiesel from less pure oil. The supercritical technology is the fastest one, also providing a good final glycerin quality that requires not much purification to reach a commercial grade. However, the reaction temperature and pressure are quite high and therefore, the cost is quite high in comparison with other technologies that are slower.

In the case of solid resin, the reaction time is variable since it has been found that this could be from an hour to several days; and therefore, there is not average range to have here. On the other hand, a solid resin does allow a good final product for biodiesel as well as glycerol and does require few number of equipment for the process. A similar case is the monolithic reactor. In this case, as pointed out before, the leaching of the catalyst from the heterogeneous phase to the homogeneous phase is a problem.

6. Conclusions

Biodiesel production is normally done by using refined oil due to the fact that the most common technology to produce biodiesel is based on a homogeneous catalyst such as sodium hydroxide. However, in order to use less pure raw material, newer technologies are needed.

As shown, the final biodiesel will have different properties based on the type of vegetable oil that is used, being the fatty acid chain the key factor to the difference among the main physical-chemical properties of the final fuel. It was also shown that the different qualities of the raw oil, such as refined, crude, and waste have a net influence also on the properties.

As presented in Table 6, the use of microalgae for oil production is a new and very promising alternative since it could grow in non-drinkable water and the oil is not used for food purpose. Even more, the amount of landscape required to produce the same amount of biodiesel that is produced now is considerably reduced due to the high efficiency of the algae.

The last point exposed is based on a comparison of the different technologies available for biodiesel production. It could be seen that each technology has advantages as well as disadvantages, making the selection of which one to use based on several points such as quality of vegetable oil, type of process desire, quality of raw material, availability and type of oil. As presented, the difference among them does not make any of these alternatives less attractive than the others; however, some of them might have some more promising future than other based on the outgoing work that is being done every day.

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