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Sustainable Biodiesel Production

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Abstract:
Current biodiesel technologies are not sustainable as they require government subsidies to be profitable by the producers and to be affordable by the public. This is mainly due to: 1) high feedstock cost and, 2) energy intensive process steps involved in their production. Sustainable biodiesel production needs to consider: a) utilizing low cost feedstock; b) utilizing energy-efficient, non-conventional heating and mixing technologies; c) increase net energy benefit of the process; and 4) utilize renewable raw material/energy sources.

In order to reduce production costs and make it competitive with petroleum diesel, low cost feedstock, non- edible oils and waste cooking oils can be used as raw materials. Net energy benefit can be increased by using high oil yielding renewable feedstock like algae. Additionally, application of energy efficient non-conventional technologies such as ultrasonics and microwaves may reduce the energy footprint of the overall biodiesel production.

This research provides a perspective on sustainable biodiesel production using waste cooking oils, non-edible and low-cost oils (*Jatropha curcas* and *Camelina Sativa*) and algae as feedstock. Process optimization using novel heating and mixing techniques, and net energy scenarios for different feedstock from sustainability view of the biodiesel production technologies are presented.

1. Introduction

1.1. Need for Renewable Fuels

The U.S. consumes over 50 billion gallons of diesel fuel per year for transportation purposes [1] and about 65% of these fuels are imported from foreign countries. In 2007, the U.S. Government Accountability Office reported the need to develop a strategy for addressing a peak and decline in oil production [2]. Declining oil production will cause oil and diesel prices to rise sharply creating a strong market for replacement fuels. Apart from this, increasing energy use, climate change, and carbon dioxide (CO_2) emissions from fossil fuels make switching to low-carbon fuels a high priority [3]. Biodiesel is an alternative liquid fuel that can substantially replace conventional diesel and reduce exhaust pollution and engine maintenance costs. This renewable fuel can be produced from different feedstocks such as soybeans, waste cooking oil, and algae. Biodiesel production has increased exponentially over the past decade due to the above mentioned reasons as shown in **Fig.1**. The world biodiesel production has increased by more than 10 times (between 2001 and 2010) while the U.S. biodiesel production has increased exponentially (by 200% every year). This increase can be directly related to the escalating gasoline and diesel prices over the past decade which are expected to rise in the future [4].
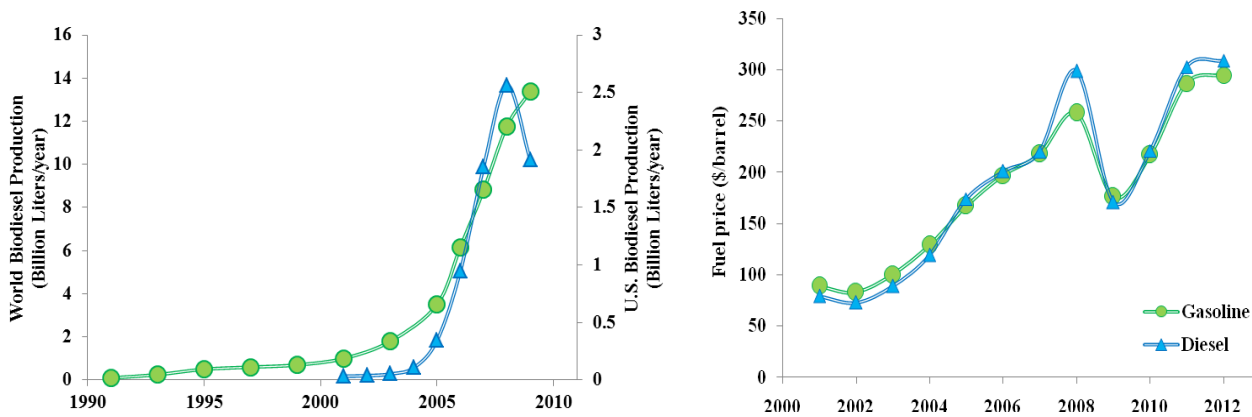

Fig. 1. (a) World and U.S. Biodiesel Production; (b) Fuel Prices Trend (2000-2012)

Local biodiesel production may play a critical role in promoting economic, energy, and environmental security of the nation. In 2007, the U.S. government has committed to increase the renewable fuel production to 36 billion gallons per year by 2022 [5]. However, current biodiesel technologies are not sustainable since they require government subsidies to be profitable for the producers and to be affordable by the public. This is mainly due to: 1) high feedstock cost (up to 75-80% of the total biodiesel cost) [6, 7] and, 2) energy intensive process steps involved in their production [8]. Most of the biodiesel in the U.S. is currently made from soybeans, which will soon reach a resource limitation of arable land. Use of natural resources for soybean biodiesel production has resulted in high food costs [9, 10] and deforestation increasing the net CO_2 emissions to increase the arable land by removing the existing forests. These situations have resulted in hot debates and were termed as "*food vs. fuel*" and "*energy vs. environment*" dilemmas [3, 11]. For example: converting rainforests, peatlands, savannas, or grasslands to produce food crop–based biofuels in Brazil, Southeast Asia, and the United States creates a "biofuel carbon debt" by releasing 17 to 420 times more CO_2 than the annual greenhouse gas (GHG) reductions that these biofuels would provide by displacing fossil fuels. In contrast, biofuels made from waste biomass or from biomass grown on degraded and abandoned agricultural lands planted with perennials incur little or no carbon debt and can offer immediate and sustained GHG advantages [3]. Also, another example: as fuel demand for corn increases and soybean and wheat lands switch to corn, prices increase by 40%, 20%, and 17% for corn, soybeans, and wheat,

respectively. As more American croplands support ethanol or biodiesel production, U.S. agricultural exports decline sharply (compared to what they would otherwise be at the time - corn by 62%, wheat by 31%, soybeans by 28%, pork by 18%, and chicken by 12%). All of this will result in increased land use in other parts of the world to balance the supplies [12].

1.2. Sustainable Biodiesel Production

For biodiesel to substitute conventional gasoline as an alternative transportation fuel should (*i*) have superior environmental benefits (*ii*) be economically competitive, (*iii*) have meaningful supplies to meet energy demands, and (*iv*) have a positive net energy balance ratio (NER) [13,14]. Biofuels are a potential low-carbon energy source, but whether biofuels offer carbon savings depends on how they are produced as explained earlier [3]. Utilizing low cost edible or non-edible feedstock such as waste cooking oils, *jatropha curcas* and *camelina sativa* oils can be an attractive alternative to reduce overall biodiesel cost. Waste cooking oils are often available at free of cost. They will need to be disposed properly or they will pose environmental threat. Waste cooking oils as feedstock offer some specific benefits as shown in **Table 1**. Camelina Sativa, Jatropha curcas and other non-edible crops are known as low maintenance and low cost crops. Few examples of non-edible oils are Jatropha oil, Karanji or Pongamia oil, Neem oil, Jojoba oil, Cottonseed oil, Linseed oil, Mahua oil, Deccan hemp oil, Kusum oil, Orange oil, and Rubber seed oil [15, 16]. Algae, on other hand, is very high oil yielding biodiesel feedstock (**Table 1**).
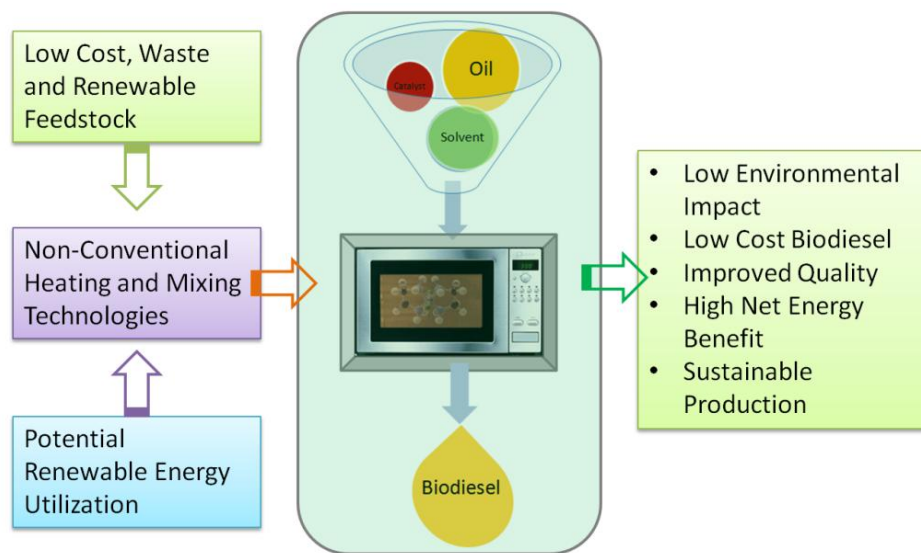

Fig. 2. Sustainable Biodiesel Production

1.3. Oils to Biodiesel Conversion

The carbon chains (triacyglycerides) in vegetable and other plant oils (including algae) are too long and too viscous for good flow and combustion. They have to be converted into low viscous fuels to serve as transportation fuels. There are many ways to achieve this, but the most commonly used method is transesterification (**Fig. 3**). This process involves addition of alcohol-catalyst mixture to convert the triglycerides into smaller hydrocarbon chains to make an alternative fuel for diesel engines. Glycerin is formed as by-product which is used in many chemical industries as raw material. The end product of the oil conversion using methyl alcohol is fatty acid methyl ester (FAME) which is called "Biodiesel". Biodiesel fuels must meet stringent chemical, physical and quality requirements imposed by the US EPA as specified in ASTM standard D6751. Biodiesel has unique properties, which include almost no sulfur or particulate matter that contribute to air pollution.

Table 1. Comparison of different feedstock and heating methods

Waste Cooking Oil		Virgin Oils	
Advantages	Disadvantages	Advantages	Disadvantages
Low cost (free or low cost feedstock)	High FFA	Low FFA	High cost feedstock (up to 80% of total cost)
No environmental pollution	High processing cost due to mass transfer restrictions	Low processing cost	Some environmental pollution due to cultivation, fertilizers and processing
High Net Energy Ratio			Low Net Energy Ratio
Algae		**Other Terrestrial Plants**	
High growth			Very slow growth
High oil yield			Low oil yield
Water recycling possible			High water requirements
Nutrient recycling possible	Complex process techniques	Simple processing	High nutrient requirements
Wastewater cultivation			Limitations apply
Environmental-friendly, removes CO_2			Some environmental pollution for cultivation
Non-Conventional Heating		**Conventional Heating**	
High efficiency (> 75%; ex: microwaves and ultrasonics)			Low efficiency (~35%; fossil fuel based, electricity to heat)
Low chemical usage			High chemical usage
Low energy consumption due to fast and easy processing	High capital costs?	Low capital costs?	High energy consumption
Precise process control	Technology know-how	Well-known and established heat sources	Complex process control
Small plant footprint		Large plant footprint	
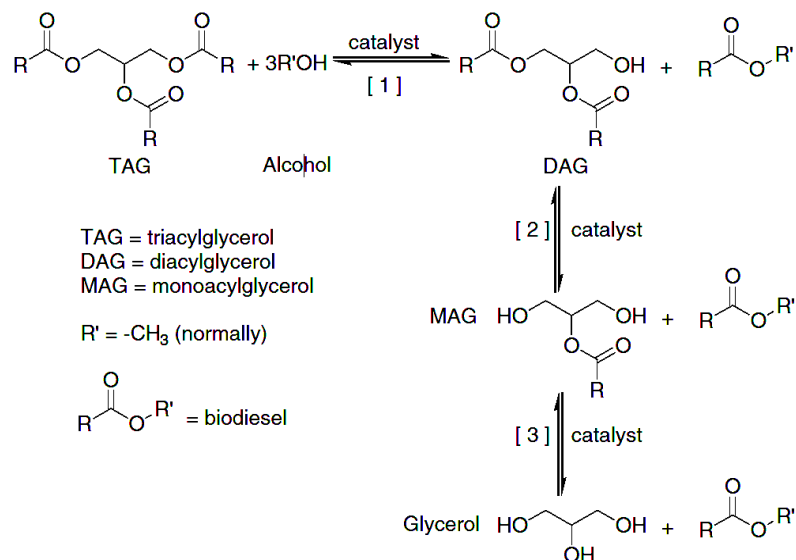
Fig. 3. Biodiesel Production by Transesterification [17]

2. Results and Discussion

In this section, process parametric optimization studies for three different feedstocks (waste cooking, *Jatropha Curcas* (non-edible) and *Camelina Sativa* (edible) oils are presented. A comparison between three process heating techniques for waste cooking oil biodiesel conversion is also presented, followed by biodiesel production from algae, comparison of conventional and non-conventional heating methods and net energy benefit ratio discussion.

2.1. Use of Low Cost Feedstock: Waste Cooking, Jatropha Curcas and Camelina Sativa Oils
The main process parameters optimized in this study are: 1) methanol to oil ratio; 2) catalyst concentration; 3) reaction temperature and 4) reaction time [18].

2.1.1. Methanol to Oil Ratio: Transesterification reaction was studied for four different molar ratios. The methanol to oil molar ratio was varied for *Jatropha Curcas* oil and waste cooking oil within the range of 3:1 to 12:1. The maximum ester conversions for *Jatropha Curcas* oil and waste cooking oil were found at the methanol to oil molar ratio of 9:1. **Fig. 4a** shows the effect of methanol to oil molar ratio on the conversion of oil. The yield remains the same with further increase in the methanol to oil molar ratio. The excess methanol in the ester layer can be removed by distillation. Therefore, the methanol to oil molar ratio was kept at 9:1 in the remaining experiments with *Jatropha Curcas* oils. For waste cooking, and *Camelina Sativa* oils similar trend was observed. The yield of the process increased with increase in methanol to oil molar ratio up to 9:1.

2.1.2. Catalyst Concentration: For *Jatropha Curcas* and waste cooking oils, acid esterification was performed using sulfuric acid and ferric sulfate as catalysts respectively, followed by alkali transesterification reaction using KOH as catalyst. The effect of alkali catalyst (KOH) was studied in the range of 0.3 % to 2.5% and 0.5% to 2% by weight for waste cooking oil and *Jatropha Curcas* oil, respectively. **Fig. 4b** shows the influence of the amount of ferric sulfate on biodiesel yield for waste cooking oil. The yield was quite low for less quantity of catalyst. The amount of catalyst required depends on the amount of free fatty acid content. In this study, the catalyst concentration of ferric sulfate to waste cooking oil was varied within a range of 0.5-2.5 %. Similarly, sulfuric acid catalyst amount was varied in the range of 0.3-2% for *Jatropha Curcas* oil. These percentages are based on the volume of the oil used for the acid esterification reaction. The catalyst amount also affects the yield of the process as shown in **Fig. 4b**. The acid-catalyst process attained maximum yield for jatropha oil at 0.5% catalyst concentration. For *Jatropha Curcas* oil, it was observed that the yield started to decline when the catalyst concentration was increased above 0.5%. For *Camelina Sativa* oil, a heterogeneous catalyst (BaO) was employed. Biodiesel yield increased initially with increased BaO concentration (0.5-1%) and remained unchanged with further increase in the catalyst concentration (>1%).

2.1.3. Reaction Temperature: In order to study the reaction temperatures, some alkali transesterification experiments were conducted at temperatures close to the boiling point of methanol [19]. As shown in **Fig. 4c**, the reaction temperature effect on the yield was studied in the temperature range of 40 to 100°C for *Jatropha Curcas* oil at atmospheric pressure. The maximum yield was obtained at a temperature of 60°C for *Jatropha Curcas* oil. A decrease in yield was observed when the reaction temperatures were above 60°C. Although other researchers have achieved optimum yield at temperatures above 60°C and 70°C while using refined linseed oil and brassica carinata oil, respectively [20, 21]. The reaction temperature for processing *Jatropha Curcas* oil should be maintained below 60°C because saponification of glycerides by the alkali catalyst is much faster than the alcoholysis at temperatures above 60°C. For waste cooking oil, the reaction temperature was studied in the range of 60 to 120 °C. The maximum biodiesel yield was obtained at 100 ºC.

2.1.4. Reaction Time: As shown in **Fig. 4d**, the optimum reaction times were determined as 120, 120 and 180 minutes for *Jatropha Curcas*, waste cooking and *Camelina Sativa* oils respectively [18, 22, 23]. *Camelina Sativa* oil was transesterified using heterogeneous metal oxide catalyst which generally

requires longer reaction times [22]. However, heterogeneous catalysts allow for successive recovery and recycling for many times without affecting the biodiesel yield and quality. Optimized process conditions are shown in **Table 2**.
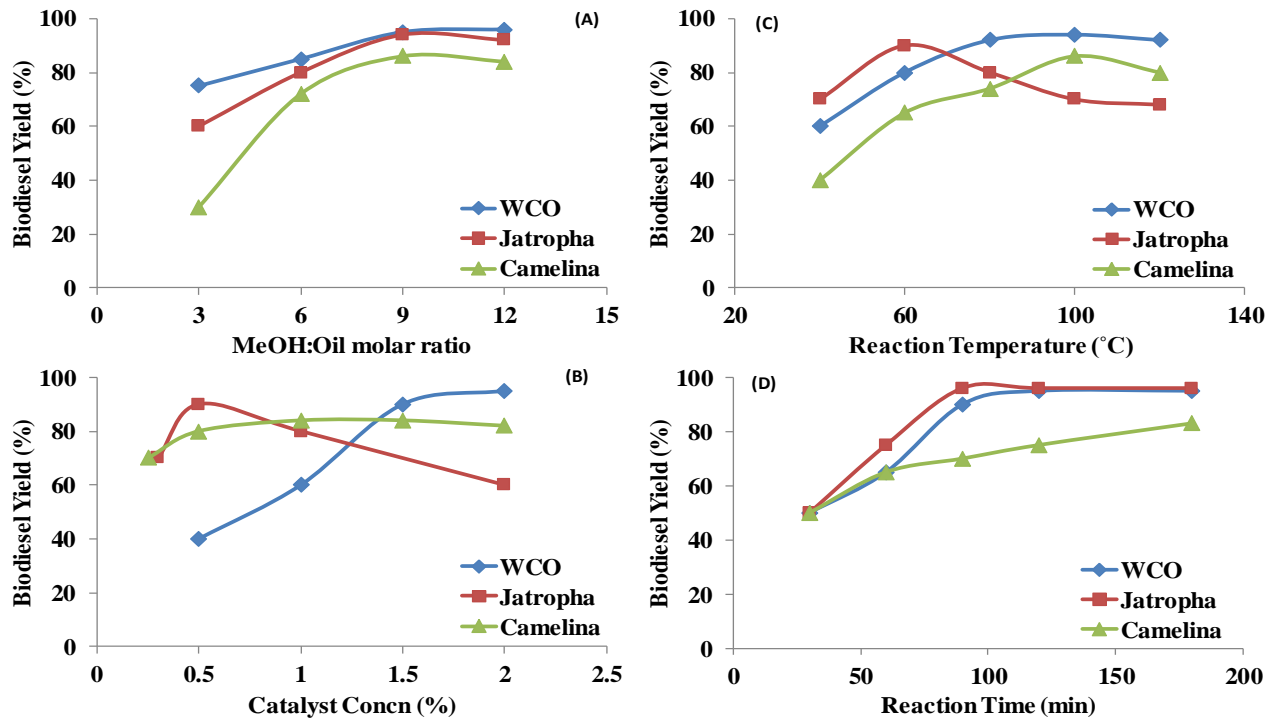

Fig. 4. Process Optimization for Waste cooking, *Jatropha Curcas* and *Camelina Sativa* oils

Table 2. Comparison of different feedstock and heating methods

Feedstock	Waste Cooking Oil	*Jatropha Curcas*	*Camelina Sativa*
Process	Two-step (step 1-acid esterification and step 2-alkali transesterification)		One-step (Alkali transesterification)
Catalyst	$Fe_2(SO_4)_3/H_2SO_4$ (Step 1), KOH (Step 2)		BaO
Optimized Parameters [MeOH:Oil, Catalyst (wt%),Temp-^{o}C, Time- min]	9:1, 100°C, 2% $Fe_2(SO_4)_3$ (step 1), 9:1, 100°C, 0.5% KOH, (step 2)	6:1, 0.5% H_2SO_4, 40±5°C (step 1), 9:1, 2% KOH, 60°C (step 2)	9:1,1%,100°C,180min
Biodiesel Yield (%)	96	90	84

2.2. Use of Renewable Feedstock

Algae

Biodiesel feedstock can be separated into three generations. First generation feedstock such as corn and soybeans cannot meet all the transportation fuel needs due to limitations in production capacity. Additionally, food vs. fuel issues, requirement of intensive agricultural inputs, land use, and freshwater use are some of the limitations for large-scale production of the first generation of biofuels. Second-generation feedstocks, using cellulose in nonedible plant biomass, address some of the concerns such

as food vs. fuel. Though (ligno) cellulosic feedstocks do not use human food resources, they still require arable land, freshwater, and some agricultural and nutrient inputs for their production [24]. Algae and other microorganism (such as cyanobacteria) based feedstock are termed as third generation feedstock. Algae are an ideal example of renewable feedstock since they are produced in very short periods of time. Microalgae are very small aquatic plants that produce natural vegetable oils suitable for conversion to biodiesel. Algae have the potential for yields 50-100 times greater than biodiesel from soybeans and other feedstock [25]. Algal cultivation can be enhanced by the direct addition of waste CO_2 from fossil-fueled power plants and other high carbon emitting facilities thus recycling and reducing environmental CO_2 emissions [1]. In addition, algal biodiesel is a carbon-neutral fuel, which means it assimilates about as much CO_2 during algal growth as it releases upon fuel combustion. Based on life-cycle analyses, biodiesel use can improve air quality; reduce atmospheric CO_2 concentrations; and decrease engine maintenance. Biodiesel fuel is easily blended with petroleum diesel to make a premium fuel with improved performance [1].

2.3. Use of Non-conventional Technologies
2.3.1. Waste cooking oil-biodiesel conversion via conventional, microwave and ultrasonic methods

We have utilized three different types of heating methods to process waste cooking oil. As discussed in section 2.1., the conventional heating method takes the longest reaction time (105 minutes). Microwaves reduce the reaction time significantly to as low as 6 minutes. The reasons for enhanced reaction rates for non-conventional heating are compared with conventional heating in **Table 3**. We have also tested direct transesterification of waste cooking oils to biodiesel by using ultrasonic irradiation. When direct sonication was applied, we noticed that the reaction mixture temperature has increased without any external heat addition. Similar effects were observed under microwave conditions as well. Reaction mixture temperatures as high as 85°C were recorded under 2 minutes of reaction time. This depends on the catalyst ratio and the reaction mixture volume [26].

Table 3. Comparison between different heating methods

Conventional heating	Microwave heating	Ultrasonic heating
Thermal gradient Conduction and Convection currents	Inverse thermal gradient Molecular level hot spots	Thermal gradient due to mixing Microbubble formation and collapse (compression and rarefaction cycles)
Longer processing times	Very short and instant heating	Relatively very short reaction times, not as quick as microwaves
No or low solvent savings	No or low solvent reactions possible	Solvent savings possible
Product quality and quantity can be affected	Higher product quality and quantity possible	Same as conventional heating
Separation times are long	Very short separation times	Less than conventional heating
High energy consumption	Moderate to low consumption	Moderate to low consumption
Complex Process configuration	Very simple process	Moderate complexity

As shown in **Fig. 5**, increased reaction times result in increased energy expenditures. As shown in Fig. 5, conventional heating on a laboratory hot plate requires about 3150 kJ of energy to perform transesterification while microwave and ultrasonic processes required 288 and 60 kJ of energy. This shows that with appropriate reactor design, non-conventional techniques have potential to reduce the process energy requirements significantly.

Another observation made among these studies is that microwave process provides high quality biodiesel product compared to other two methods of biodiesel conversion. Convectional and ultrasonic based transesterification involves intense mixing of reaction mixture thus resulting in increased separation times, and reduced product yield and quality.
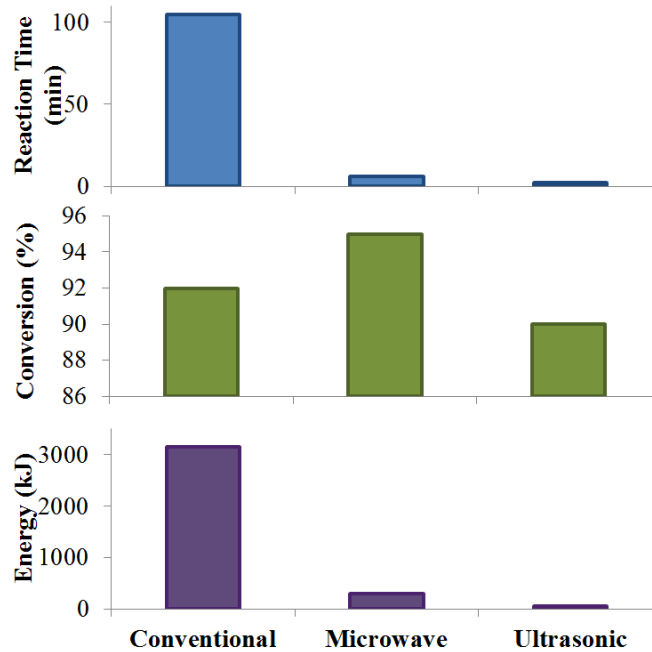

Fig. 5. Comparison of waste cooking oil conversion by conventional/non-conventional methods

2.3.2. Algal biomass conversion via microwave process

Algae can be processed in both wet and dry forms [27, 28]. Wet algal biomass conversion into biodiesel can be processed by exploiting the specific characteristics of water at supercritical conditions. Methanol can be used as a solvent to extract algal oils as well as to achieve transesterifiction. Algae, in its dry form, can be processed via non-conventional techniques (like microwaves and ultrasonics). A microwave based dry algal process scheme is shown in **Fig. 6**.
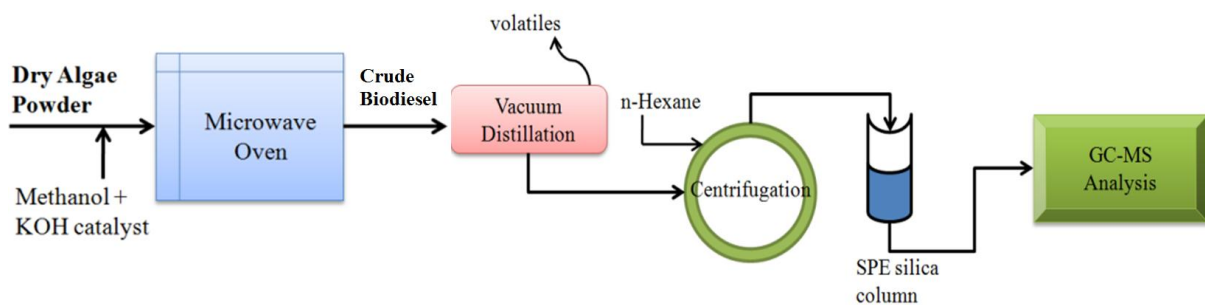

Fig. 6. Algal biomass conversion via microwave process

A response surface methodology was used to optimize the dry algal biomass conversion under microwave irradiation. The response contours for the effect of different process parameters namely algae to methanol (wt./vol.) ratio, catalyst concentration expressed as wt.% of dry algae, and reaction time (min) on the fatty acid methyl ester (FAME) contents were studied. The effect of methanol on the

simultaneous extraction and transesterification reaction is significant with increasing dry algae to methanol ratios up to 1:12 (wt./vol.). In this reaction, methanol acts both as a solvent for extraction of the algal oils/lipids as well as the reactant for transesterification of esters. Methanol is a good microwave radiation absorption material (loss factor, tand = 0.659 at 2.45 GHz) which absorbs most of the microwave effect in its entire spectrum to produce localized superheating in the reactants and assists the reaction to complete faster. However, higher volumes of methanol may also result in excess loss of the solvent or aggravated rates of solvent recovery. In addition, excessive methanol amounts may reduce the concentration of the catalyst in the reactant mixture and retard the transesterification reaction [28]. Catalyst concentrations up to 2% (KOH, wt.%) shows a positive effect on the transeseterification reaction. As this is two-phase reaction mixture, the oil/lipid concentration in the methanol phase is low at the start of the reaction leading to mass transfer limitations. As the reaction continues, the concentration of oil/lipid in the methanol phase increases, leading to higher transesterification rates with increased catalyst concentrations [29]. However, higher concentrations of catalyst above 2% (wt.%) did not show any positive effect on the biodiesel conversion. This may be due to the interaction of the other compounds resulting in byproducts. Other disadvantages of high basic catalyst concentrations, in general, are their corrosive nature and tendency to form soap which hinders the transesterification reaction [30]. The reaction time has a significant effect on the FAME content. Generally, extended reaction times provide for enhanced exposure of microwaves to the reaction mixture which result in better yields of extraction and biodiesel conversion. Lower reaction times do not provide sufficient interaction of the reactant mixture with microwaves to penetrate and dissolve the oils into the reaction mixture. The main advantage of using microwave accelerated organic synthesis is the shorter reaction time due to rate enhancement. The rate of reaction can be described by the Arrhenius equation as: $K = Ae^{-\Delta G/RT}$, where 'A' is a pre-exponential factor, 'ΔG' is Gibbs free energy of activation. The rate of chemical reaction can be increased through the pre-exponential factor A, which is the molecular mobility that depends on the frequency of the vibrations of the molecules at the reaction interface [31] or the pre-exponential factor can be altered by affecting the free energy of activation [32, 33]. A reaction time of 5-6 minutes was found to be sufficient for this method with high FAME yields of >80%.

2.4. Increase Net Energy Benefit Ratio (NER)

2.4.1. Overall Scenario

Energy is expended in various steps of biodiesel production including steps: 1) cultivation; 2) feedstock processing; 3) oil extraction; 4) oil conversion into biodiesel; and 5) separation and purification. **Table 4** shows net energy ratios for different fuel and biodiesel types [34].

Table 4. Comparison between different heating methods

Fuel Type	NER	Reference
Petroleum diesel	0.83	[35, 36]
Corn ethanol	1.34	[37]
1st Generation bio-diesel	1.98 (Only RME[a])	From oilseed rape,
	3.45 (RME + meal + glycerin)	UK [38]
	1.84 (only bio-diesel)	From soybean, USA
	3.2 (Biodiesel + meal)	[35, 36]
	2.42 (Only PME[b])	From palm, THA
	3.58 (PME + meal + glycerol)	[39]
Algal fuel	1.87[c]	[40]
	1.50[d] (2.38[e])	[34]
	1.37[d] (1.82[e])	[34]

[a] Rapeseed methyl ester; [b] Palm methyl ester; [c] Lipid productivity = 20 ton ha_1 year_1; [d] The base case;

[e] Assuming low temperature (<100 _C) heat is available from an upstream fossil fuel combustion process.

2.4.2. Algae as a Case Study

Algal biodiesel production can be sustainable only if net energy gain from the entire process is a positive value or higher than one. The net energy ratio is defined as the ratio of the energy available from the end product (algal biodiesel) to the energy invested in the conversion process. Algae have energy content of 5-8 kWh/kg (18000-28800 kJ) of dry weight depending on the species and lipid content [41]. Therefore, in order for algal biodiesel production to be feasible, the amount of energy required to produce the algae and process it into useable fuel must be less than this amount [42]. Energy ratio can be written as:

$$E_{NER} = \frac{E_{out}}{E_{in}} = \frac{Energy\_in\_Alg\,albiofuel}{Energy\_invested}$$

Fig. 7 shows the energy requirements for algal biodiesel production. Cultivation and algal biomass production alone consumes around 15% of the total energy and major energy consumption (~60%) by harvesting and drying steps to prepare dry biomass suitable for transesterification reaction. This suggests alternative methods for drying the algae or eliminating the need for drying. Supercritical or other hydrothermal processes will need to be employed for direct wet algal biomass conversion into biodiesel. **Table 5** summarizes the energy inputs and the net energy benefit ratios reported by other researchers
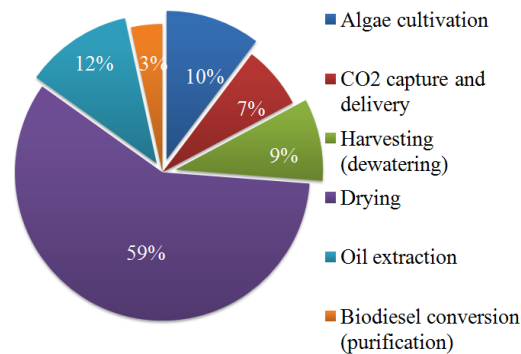

Fig. 7.Energy requirements for algal biodiesel production reported by recent studies

Table 5. Energy inputs and net energy ratios for algal biodiesel production [40, 41, 43, 44]

Energy required for each operation (GJ/ton)	Sturm &Lamer 2011	Batan et al. 2010	Lardon et al. 2009	Stephenson et al. 2010
Cultivation	9.7	0.8	5.7	7.2
Flocculation	3.0			0.5
Centrifugation	15.0	10.7	–	2.0
Belt filter press	12.2		11.9	–
Oil extraction				
Electricity	–	21.8	3.9	0.3
Heat	–	–	10.2	2.3
Lipid conversion				
Electricity	–	9.7	–	0.2
Heat	–	–	0.9	1.6
Net energy ratio*		**0.66**	**0.88**	**2.04**

*based on 28800 kJ of energy per kg of algal biomass

2.5. Use of Renewable Energy Sources

Utilizing renewable energy sources may bring down the GHG emissions as their payback periods are very reasonable (less than 2 years) for both energy and emissions in many cases [45, 46]. Moreover, the cost of these renewable energy sources has become competitive with other conventional fossil fuel based energy. A variety of renewable energy sources such as solar collectors, geothermal wells and wind turbines can be used to provide for the energy needs of biodiesel production. However, selection and application of these resources can be site-specific and the economics may vary in a wide scope as the economical packages are different for each geographical location in the world.

3. Experimental Section

3.1. Waste Cooking, Jatropha Curcas and Camelina Sativa Oils

Waste cooking oil was collected from a local restaurant in Las Cruces, NM, U.S.A. Cold-pressed *Camelina Sativa* oil was obtained from Marx Foods Company, New Jersey, U.S.A. *Jatropha Curcas* oil was obtained from Purandhar Agro & Biofuels (Pune, India). Potassium hydroxide flakes, methanol (AR Grade), and chloroform were procured from Fisher Scientific. The ferric sulfate catalyst was obtained from MP Biomedical. Heterogeneous metal oxide catalyst (BaO) was purchased from Alfa Aesar. To test the physio-chemical properties of oil, ethanol (95% v/v), hydrochloric acid and diethyl ether were purchased from Fisher Scientific. A round-bottom flask with reflux condenser arrangement was used as laboratory scale reactor for the experimental studies in this work, and a hot plate with magnetic stirrer was used for heating the mixture in the flask. For transesterification of oil, the mixture was stirred at the same agitation speed of 1000 rpm for all test runs. A domestic microwave unit (800 W power) and Sonic dismembrator (Model 550 from Fisher Scientific, 500W and 20 kHz) were used for microwave and ultrasonic based tranesterification reactions.

Jatropha Curcas and waste cooking oils conversion consists of two steps namely, acid esterification and alkali transesterification. For a successful reaction, the waste cooking oils must be heated above 100 °C for 1 hour to remove the water and other impurities. Its free fatty acid (FFA) content was determined by a standard titrimetry method. After the reaction, the mixture was allowed to settle for eight hours in a separating funnel. The acid value of the pretreated oil from step 1 was determined. The pretreated oil having an acid value less than 2 ± 0.25 mg KOH/g was used for the main transesterification reaction.

For *Jatropha Curcas* oil, in acid esterification, 25 mL of oil was poured into the flask and heated to about 45ºC. Then 8 mL of methanol was added and stirred at low stirring speed for 10 minutes followed by 0.5% (v/v) of sulfuric acid. The reaction mixture was then poured into a separating funnel to remove excess alcohol, sulfuric acid and impurities. The experimental set-up for alkali catalyzed transesterification was the same as that used for the acid esterification. 0.45 g (2 %) of KOH was dissolved in 10 mL of methanol and half of that was poured into the flask containing unheated mixture from acid esterification step and stirred for 10 minutes. After 10 minutes, the mixture was heated and stirred continuously to about 60 ºC, and then the remaining methoxide was added to it. The reaction was continued for the next 2 hours.

For *Camelina Sativa* oil, a single step alkali transesterification was conducted with heterogeneous metal oxide catalyst, BaO. The experimental plan involved five levels of methanol to oil ratio varying from 3:1 to 15: 1; five levels of catalyst concentration, 0.25, 0.5, 1, 1.5, 2 (%,w/w, oil); five levels of reaction time, 0.5,1 ,1.5, 2 , 3 h; and five levels of reaction temperature varying from 40 to 130ºC.

3.2. Dry Algae

The experimental protocol for single-step microwave-assisted extraction and transesterification process for dry algal biomass is illustrated in **Fig. 6**. Wet algal biomass was allowed to dry in a laboratory vacuum oven at 50–60˚C for 24 h. Dry algal powder was obtained by treating the algal biomass with liquid Nitrogen and rupturing it in the laboratory grinder. Two grams of dry algae powder were added to the premixed homogeneous solution of methanol and KOH catalyst. The mixture was then subjected to the microwave irradiation with exiting power of 800W (power dissipation level of 50% = 400 W), under a matrix of conditions: reaction times of 3, 6, and 9 min; catalyst concentrations in the range 1–3 wt.% of dry biomass; and dry algae to methanol (wt./vol.) ratios of 1:9–1:15. After the reaction was completed, the reactor contents were transferred into a 50 mL round-bottom flask to remove methanol and volatile compounds at a reduced pressure in a rotary evaporator. The remaining products were taken in hexane-water mixture and then centrifuged (3200 rpm) for 5 min to induce biphasic layer. The upper organic layer containing non-polar lipids was extracted and run through a short column of silica (Hyper SPE silica) (**Fig. 6**). Neutral components were eluted with the solvent. An internal standard, methyl heptadecanoate (C17:0) was added to the eluted neutral component-solvent solution and analyzed by gas chromatography-mass spectroscopy GC–MS and FT-IR.

4. Conclusions

Biodiesel can be produced with minimum environmental pollution by using low cost and renewable feedstock. This paper illustrated methods for sustainable biodiesel production from various feedstock. Net energy benefit of the biodiesel production process can be increased by using high oil yielding and low energy consuming feedstock (low maintenance, low water consumption). Biodiesel production costs can be reduced by utilizing locally available used cooking oils and by utilizing process by-products as raw materials in other chemical processes. Utilizing renewable feedstock such as algae will reduce the environmental emissions and facilitate nutrient recovery and wastewater reuse and recycling. Non-conventional technologies such as microwaves and ultrasonics have potential to reduce the energy footprint of the biodiesel processes.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

1. Gallagher, B.J. The economics of producing biodiesel from algae. *Renewable Energy* **2011**, *36*, 158-162.
2. US Government Accountability Office. Crude oil: uncertainty about future oil supply makes it important to develop a strategy for addressing a peak and decline in oil production. US Government Accountability Office; 2007
3. Fargione, J.; Hill,J.; Tilman, D.; Polasky, S.; Hawthorne, P. Land Clearing and the Biofuel Carbon Debt. *Science* **2008**, *319* (29), 1235-1238.

4. US Energy Information Administration. US energy outlook, Table A11. Liquid fuels: biodiesel. Report #DOE/EIA-0383(2009). Available at: http://www.eia.doe.gov/oiaf/aeo/pdf/0383(2009).pdf; 2009 (accessed September 2009).

5. Energy Independence and Security Act of 2007 (EISA 2007): Summary of Provisions. http://www.eia.gov/oiaf/aeo/otheranalysis/aeo_2008analysispapers/eisa.html

6. Zhang, Y.; Dube, M.A.; McLean, D.D.; Kates, M. Biodiesel production from waste cooking oil: 2.Economicassessment and sensitivity analysis. *Bioresource Technology* **2003**, *90*, 229–40.

7. Berrios, M.; Martin, M.A.; Chica, A.F.; Martin, A. Purification of biodiesel from used cooking oils. *Applied energy* **2011**, *88* (11), 3625-31.

8. Leung, D.Y.C.; Wu, X.; Leung, M.K.H. A review on biodiesel production using catalyzed transesterification. *Applied energy* **2010**,*87* (4), 1083-95.

9. Radich, A. Biodiesel Performance, Costs, and Use.US Energy Information Administration, 2006. http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/idexhtml

10. Balat, M.; Balat, H. Progress in biodiesel processing. *Applied energy* **2010**, *87* (6), 1815-35.

11. Santori, G.; Nicola, G.D.; Moglie, M.; Polonara, F. A review analyzing the industrial biodiesel production practice starting from vegetable oil refining. Applied energy 2012; 92:109-32.

12. Searchinger, T.; Heimlich, R.; Houghton, R. A.; Dong, F.; Elobeid, A.; Fabiosa, J.; Tokgoz, S.; Hayes, D.; Yu, T. Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change. *Science* **2008**, *319* (29), 1238-1240.

13. Hill, J.; Nelson, E.; Tilman, D; Polasky, S.; Tiffany, D. *Proc Natl Acad Sci* **2006,** *103*,11206–11210.

14. Schmer, M.R.; Vogel, K.P.; Mitchell, R.B.; Perrin, R.K. Net energy of cellulosic ethanol from switchgrass. *Proc Natl Acad Sci* **2008**, *105* (2), 464-469.

15. Vasudevan, P.T.; Briggs, M. Biodiesel production—current state of the art and challenges *J Ind Microbiol Biotechnol* **2008**, DOI 10.1007/s10295-008-0312-2.

16. Hossain, A.K.; Davies, P.A. Plant oils as fuels for compression ignition engines: A technical review and life-cycle analysis. *Renewable Energy* **2010**, *35*, 1–13

17. Moser, B.R. Biodiesel production, properties, and feedstocks. *In Vitro Cell.Dev.Biol.—Plant* **2009**, *45*, 229–266.

18. Patil, P.D.; Gude, V.G.; Deng, S.Biodiesel Production from Jatropha Curcas, Waste Cooking, and Camelina Sativa Oils *Ind. Eng. Chem. Res.* **2009,** *48,* 10850–10856

19. Srivastava, A.; Prasad, R. Triglycerides-based diesel fuels. *Renewable Sustainable Energy Re*V. **2000**, *4*, 111.

20. Dorado, M. P.; Ballesteros, E.; Almeida, J. A.; Schellert, C.; Lohrlein, H. P.; Krause, R. An alkali-catalyzed transesterification process for high free fatty acid waste oils. *Trans. ASAE* **2002**, *45*, 525.

21. Van Gerpen, J. Biodiesel processing and production. *Fuel Process. Technol.* **2005**, *86*, 1097.

22. Patil, P.D.; Gude, V.G.; Camacho, L.M.;Deng, S. Microwave-Assisted Catalytic Transesterification of Camelina Sativa Oil.Energy Fuels 2010; 24: 1298–304.

23. Patil, P.D.; Gude, V.G.; Reddy, H.K.; Muppaneni, T.; Deng, S. Biodiesel Production from Waste Cooking Oil Using Sulfuric Acid and Microwave Irradiation Processes. *Journal of Environmental Protection* **2012,** *3*, 107-13.

24. Sander, K.; Murthy, G.S. Life cycle analysis of algae biodiesel. *Int J Life Cycle Assess* **2010**, *15*,704–714

25. Chisti, Y. Biodiesel from microalgae. *Biotechnol Adv* **2007**, *25*, 294–306

26. Gude, V.G.; Grant, G.E. Biodiesel from waste cooking oils via direct sonication, *Applied Energy*, Under Review

27. Gude, V.G.; Patil, P.D.; Deng, S.; Nirmalakhandan, N. Microwave enhanced methods for biodiesel production and other environmental applications. In:Sanghi R and Singh V, editors. Green Chemistry for Environmental Remediation, New York: Wiley Interscience, 2011, p.209-49.

28. Patil, P.D.; Gude, V.G.; Mannarswamy, A; Cooke, P.; Nirmalakhandan, N.; Lammers, P.; Deng, S. Comparison of direct transesterification of algal biomass under supercritical methanol and microwave irradiation conditions. *Fuel* **2012**, *97*, 822-831.

29. Zhang, S.; Zu, Y.G.; Fu, Y.J.; Luo, M.; Zhang, D.Y.; Efferth, T. Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst. Bioresour Technol 2010;101:931–6.

30. Boocock, G.B.; Konar, S.K.; Mao, V.; Lee, C.; Eiiligan, S. Fast formation of high-purity methyl esters from vegetable oils. *Am Oil Chem Soc* **1998**,*75*,1167–72.

31. Leadbeater, N.E.; Barnard, T.M.; Stencel, L.M. Batch and continuous-flow preparation of biodiesel derived from butanol and facilitated by microwave heating. *Energy Fuel* **2008**, *22*, 2005–8.

32. Lidstrom, P.; Tierney, J.P.; Wathey, B.; Westman, J. Microwave assisted organic synthesis – a review. *Tetrahedron* **2001**,*57*, 9225–83.

33. Berlan, J.; Giboreau, P.; Lefeuvre, S.; Marchand, C. Organic-synthesis in microwave field – 1st example of specific activation under homogeneous conditions. *Tetrahedron Lett* **1991**,*32*,2363–6.

34. Xu, L.; Brilman, D.W.F.; Withag, J.A.M.; Brem, G.; Kersten, K. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. *Bioresource Technology* **2011**, *102*, 5113–5122

35. Sheehan, J.; Camobreco, V.; Duffield, J.; Graboski, M. H. S. **1998.** An Overview of Biodiesel and Petroleum Diesel Life Cycles. National Renewable Energy Laboratory (NREL), Report NREL/TP-580-24772.

36. Sheehan, J.; Dunahay, T.; Benemann, J.; Roessler, P. **1998**. A Look Back at the US Department of Energy's Aquatic Species Program: Biodiesel from Algae. National Renewable Energy Laboratory (NREL), Report NREL/TP-580-24190.

37. Shapouri, H.; Duffield, A.J.; Wang, M. **2002**. The Energy Balance of Corn Ethanol: An Update. United States Department of Agriculture (NRDA), Office of the Chief Economist, Office of Energy Policy and New Uses.

38. USDA, **2003**. EU: Biodiesel Industry Expanding Use of Oilseeds. Production Estimates and Crop Assessment Division, Foreign Agricultural Service, last accessed 23rd August 2010 at <http://www.fas.usda.gov/pecad2/highlights/2003/09/biodiesel3/>.

39. Pleanjai, S.; Gheewala, S.H. Full chain energy analysis of biodiesel production from palm oil in Thailand. *Appl. Energy* **2009,** *86*, S209–S214.

40. Stephenson, L.A.; Kazamia, E.; Dennis, S.J.; Howe, J.C.; Scott, A.S.; Smith, G.A. Life-Cycle Assessment of Potential Algal Biodiesel Production in the United Kingdom: A Comparison of Raceways and Air-Lift Tubular Bioreactors. *Energy Fuels* **2010**, *24* (7), 4062-4077.

41. Lardon, L.; Helias, A.; Sialve, B.; Steyer, J.; Bernard, O. Life-cycle assessment of biodiesel production from microalgae. *Environ Sci Technol* **2009**,*43*, 6475–81.

42. Janulis, P. Reduction of energy consumption in biodiesel fuel life cycle. *Renewable Energy* **2004**, *29*,861–871

43. Sturm, B.S.M.; Lamer, S.L. An energy evaluation of coupling nutrient removal from wastewater with algal biomass production. *Applied Energy* **2011**, *88* (10), 3499-3506.

44. Batan, L.; Quinn, J.; Wilson, B.; Bradley, T. Net Energy and Greenhouse Gas Emission Evaluation of Biodiesel Derived from Microalgae. *Environ. Sci. Technol.* **2010**, *44,* 7975–7980.

45. Ardente, F.; Beccali, G.; Cellura, M.; Brano, V. Life cycle assessment of a solar thermal collector: sensitivity analysis, energy and environmental balances. *Renew Energy* **2005**, *30*,109–30.

46. Ardente, F.; Beccali, G.; Cellura, M.; Brano, V. Life cycle assessment of a solar thermal collector. *Renew Energy* **2005**, *30*,1031–54.