Green Technology: Overview on Biodiesel

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Abstract:

Petroleum-derived diesel which is increasingly called as petrodiesel is generally used as liquid fuel in diesel engines. But it is obtained from crude oil which is one of the non-renewable source of energy and it is hazardous to the environment also due to emission of gases such as carbon monoxide during combustion. Because of its non-renewable origin its sources are decreasing whereas its prices are increasing day by day so we have to search for an alternative which can be used as replacement for petrodiesel in future. One such alternative is Biodiesel which can directly replace petrodiesel. Biodiesel refers to vegetable oil or fat-based diesel fuel formed by tranesterification reaction and consisting of long oil alkyl esters mainly methyl esters. It is clean burning, biodegradable, non-toxic, environmental friendly. Jatropha is the main feedstock for biodiesel production. Currently biodiesel production is done by homogenous base catalysis reaction, but by new emerging technology for biodiesel production and its environmental friendly nature it will become one of the major energy source in future.

Keywords: biodiesel, transesterification, supercritical methods, blending.

Introduction:

As energy demand continues to increase and reserves of fossil fuels shrink, the diversification of energy sources becomes increasingly important. Several studies have presented promising methods that make use of triglycerides as an alternative fuel for diesel engine. The higher molecular weight, higher viscosity, poor cold flow properties, are the main impediments to using vegetable oil or vegetable oil blend , directly as fuel. Hence vegetable oil derivatives, mainly methyl esters, have become popular biofuel and it is known as biodiesel. [4] , [11]

Biodiesel:

Biodiesel refers to vegetable oil or fat-based diesel fuel formed by tranesterification reaction and consisting of long oil alkyl (methyl, propyl or ethyl) esters. [13]

3. Biodiesel Worldwide:

3.1. Global Scenario: Several countries especially United State and members of European Union are actively supporting the production of biodiesel from the agriculture sector. In 2006, nearly 6.5 billion liters of biodiesel was produced globally. However, by the year 2020, it is predicted that biodiesel production from Brazil, China, India and some South East Asia countries such as Malaysia and Indonesia could contribute as much as 20%. [06]

3.2. Indian Scenario: India imports more than 40% of its edible oil requirement and hence non-edible oils are used for the development of biodiesel. India is a agrarian nation and has rich plant biodiversity which can support the development of biodiesel. Common non-edible oil bearing plants and trees include neem, karanja, mahua, jatropha, etc. where Jatropha curcas and pongamia pinnata (Karanja) are gaining prominence as feed-stock for biodiesel. Jathropha carcus is main raw material for biodiesel production. [07] , [08] , [20]

4. Biodiesel, petrodiesel and blends of biodiesel : [1]

4.1. Table 1 - Difference between biodiesel and petrodiesel

Biodiesel	**Petrodiesel**
Biodiesel is produced from vegetable oils by converting the triglyceride oils to methyl (or ethyl) esters via a process known as transesterification.	Petroleum diesel, in contrast, is made up of hundreds of different hydrocarbon chains (roughly in the range of 14-18 carbons in length),

	with residues of sulfur and crude oil remaining and obtained from crude oil.
Better lubricity. The higher lubricity enable the engine to work in a smoother manner and because it works better it reduce the physical deterioration of the engine.	Less lubricity.
Lower vapor pressure and flammability than their petroleum.	Higher vapor pressure and flammability
Cleaner Burning	Not clear burning
Biodegrades much faster than petrodiesel.	Biodegrades less faster than biodiesel
Higher lubricity and cetane than petrodiesel. Because of higher cetane rating engine noise and ignition cocking get reduced.	Lower lubricity and cetane than Biodiesel.
Formed from vegetable oil resources which are infinitely grown and produced as compared to crude oil resources which are limited.	Formed from crude oil resources which are limited in nature as compared to vegetable oil.
Supporing agriculture industry.	Non supporting to agriculture industry.
Flash point = 150^0 c	Flash point = 77^0 c

4.2. Biodiesel Blends :

The level of blending with petroleum diesel is referred as Bxx, where xx indicates the amount of biodiesel in the blend (i.e. B10 blend is 10% biodiesel and 90% diesel) [07]

5. Properties of Biodiesel : [2]

Table 2 - PROPERTIES OF BIODIESEL

Specific gravity	0.87-0.89
Kinematic viscosity at 40^0c	3.7-5.8
Cetane number	46-70
Higher heating value (btu / lb)	16928-17996
Sulphur wt %	0.0-0.0024
Cloud point (^{0}c)	-11 to 16
Pour point (^{0}c)	-15 to 13
Iodine number	60-136
Lower heating value (btu / lb)	15700-16735
Density at 90^0 c	~0.900 gm/cm^3
Flash point (^{0} c)	130^0 c(min)
Methanol (% wt)	0.3
Free glycerin (wt %)	0.020
Total glycerin (wt %)	0.25

6. Biodesel production :

Process description of production of biodiesel :

6.1.1. The first step in the recovery of oil from oil seed. “crush” the seeds and then to separate oil from the residual seed material (meal).

6.1.2. The pretreated oils and fats are then mixed with alcohol and a catalyst.

6.1.3. KOH / NaOH is mixed with methanol in catalytic reactor (for 10 min) until KOH has completely dissolve and solution becomes potassium methoxide.

6.1.4. Then vegetable oil mixed for 60 minutes. i.e esterification process, then it transfer into settling tank where it settle for 6-18 hrs.

6.1.5. After this glycerin is removed from the bottom of settling tank by draining or pumped out into glycerin container.

6.1.6. From upper part of settling tank, biodiesel is removed out which is go for washing.

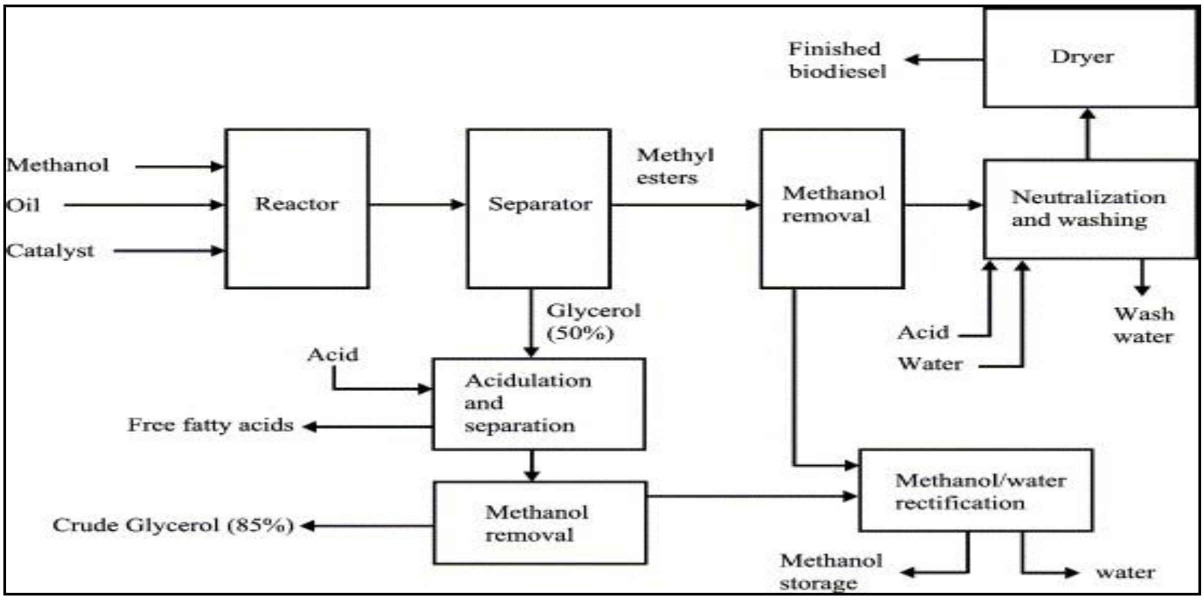
6.1.7. Excess methanol in biodiesel is removed using either vaccum or heating.

6.1.8. Acidic water washing is given (tannic or acetic acid) to remove excess catalyst.

6.1.9. Again separation is carried out and water is removed from the bottom.

6.1.10. Then product (biodiesel) is dried using heat / stirring / aeration. [01] , [17

Fig. 1 – Block Flow Diagram for biodiesel production



Transestrification:

Transesterification is the process of exchanging the organic group R" of an ester with the organic group R' of an alcohol. These reactions are often catalyzed by the addition of an acid or base catalyst. Nowdays enzymatic catalyst are also used. [05] ,[06]

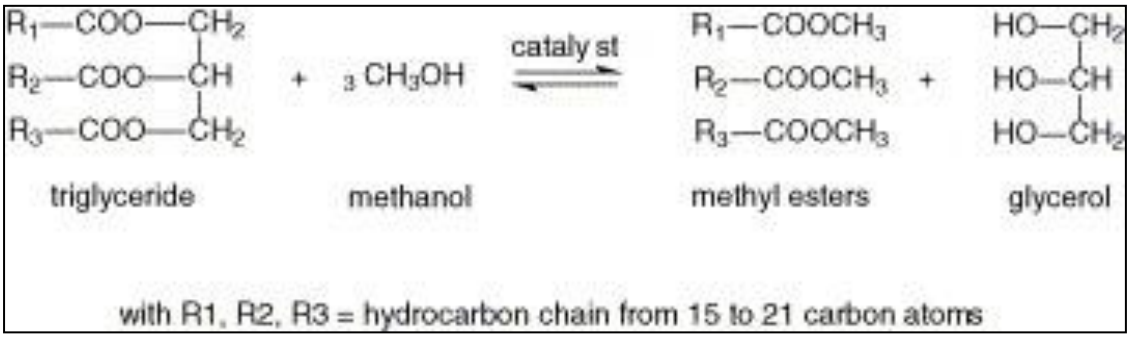


Fig 2 - Transesterification Reaction

Process variable in transestrification:

6.3.1. Reaction tempreture : Maximum yield of biodiesel obtained at 60-80^0 c. As oil tempreture increases the % oil to biodiesel conversion increases, Biodiesel recovery increases. Maximum operating tempreture is 60^0 C because at higher tempretures methanol loss can occur.

6.3.2. Ratio of alcohol to oil : At molar ratio 6:1 yield obtained is more than 98%. At theoretical stiochometric ratio 3 : 1 the yield of ester decreases to 82%. With higher molar ratio, conversion increases but recovery decreases due to poor separation of glycerin.

6.3.3. Type and concentration of catalyst : Addition of catalyst with 0.5-1 by wt% yields 94-99% conversion of vegetable oil into ester.

6.3.4. Intensity of mixing and purity of reactant

6.3.5. A small amount of water (0.1%) in the transesterification reaction would decrease the ester conversion from vegetable oil. [1] , [21]

6.3.6. Free fatty acids (FFAs) content after acid esterification should be minimal or otherwise less than 2% FFAs. These FFAs react with the alkaline catalyst to produce soaps instead of esters. [01] ,[06] ,[19]

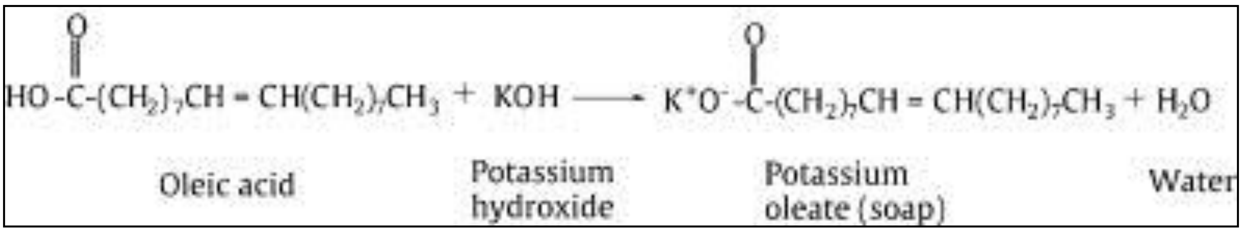


Fig 3 - Reaction of fatty acid with alkaline catalyst (soap formation) [06]

7. Biodiesel Production from Algae :

While a number of bio-feedstock are currently being experimented for biodiesel production, algae have emerged as one of the most promising sources for biodiesel production. Algae yields could reach a high of 50 T of biodiesel per hectare year against 2T for competing feedstock such as jatropha. Oil content of some microalgae exceeds 80% of the dry weight of algae biomass. Another important advantage of microalgae is that, unlike other crops, they grow extremely rapidly and commonly double their biomass within 24 hrs. [03]

8. Stability of Biodiesel :

Oxidation of biodiesel by contact with air and metal surface results in the formation of hydroperoxide. These induce free radical chain reaction that leads to decomposition into low molecular highly oxidized species (aldehyde, ketone, acid) and high M.W polymeric material (gums). These gums causes poor combustion and other engine problem such as deposits on injectors and pistons & fuel-filter plugging.

Two pronged approaches have been adopted for improving oxidation stability of Jatropha biodiesel. First route deals with the doping of Jatropha methyl esters with stabilizer or antioxidants. Among stabilizers utilized in industry phenolic antioxidants are most important. [06]

As antioxidants are costly chemicals. Therefore, another method is blending. For example, blend Jatropha oil methyl ester with palm oil methyl ester, which has good oxidation stability. The reason for good stability is the resistance to autoxidation, which was primarily due to the presence of saturated fatty acids. Jatropha has mainly unsaturated fatty acids like linoleic acid, oleic acid etc. Jatropha biodiesel, when blended with palm methyl ester leads to a composition having efficient and improved low temperature property as well as good oxidation stability. The feedstock for the synthesis of biodiesel must have a suitable combination of saturated as well as unsaturated fatty compounds to achieve improved oxidation stability and low temperature properties. [11] , [23]

9. Advantages of Biodiesel :

9.1 Produced from renewable energy sources such as vegetable oil, fats etc. so biodegradable in nature.

9.2. Biodiesel contains oxygen, so there is an increased efficiency of combustion**.**

9.3. Carbon monoxide gas is a toxic byproduct of all hydrocarbon combustion that is also reduced by increasing the oxygen content of the fuel. More complete oxidation of the fuel results in more complete combustion to carbon dioxide rather than leading to the formation of carbon monoxide.

9.4. Biodiesel helps to reduce Greenhouse Gases. The carbon dioxide released this year from burning vegetable oil Biodiesels, in effect, will be recaptured next year by crops growing in fields to produce more vegetable oil starting material.

9.5. The absence of sulfur means a reduction in the formation of acid rain by sulfate emissions that generate sulfuric acid in our atmosphere. [01]

Table 3 - Emission data for 100% biodiesel and biodiesel blends is given in table

Emmision	B_{100}	B_{20}
REGULATED EMISSION :		
Total unburned hydrocarbon	-93%	-30%
CO	-50%	-20%
Particulate matter	-30%	-22%
NO_X	+13%	+2%
NON REGULATED EMISSION :		
sulphate	-100%	-20%
PAH	-80%	-13%

[21]

10. Applications of biodiesel:

10.1. Biodiesel is used as a fuel. [01]

10.2. Biodiesel is used as a green solvent for polymerization. [12]

10.3. Dissolution of waste plastic in biodiesel is also possible. [09]

11. Cost of biodiesel :

Raw material and production cost are keeping the retail price of biodiesel too high. The recovery of higher quality glycerol, a byproduct which is required for many other processes would also contribute to substantially reducing production costs. The high cost of refined vegetable oils, currently used for the biodiesel production with the conventional base catalytic method, is the main reason for this impediment. The cost of refined vegetable oils contributed to nearly 80% of the overall biodiesel production cost . In order to overcome this limitation, biodiesel manufacturer are focusing their attention on using low-cost feedstock such as waste cooking oil in order to ensure economic viability in biodiesel production. [06]

12. Disadvantages of biodiesel:

12.1. NO_X emissions are higher which causes ozone layer destruction.

12.2. Engine performance (fuel economy, torque and power) is less than of diesel 8% to 15% because of the lower energy content of biodiesel.

12.3. Since its pour point and cloud point is around $(-10)^0$c it solidifies at that tempreture during winter in European and American countries. [01], [25]

13. Recent methods of biodiesel production :

13.1. Reaction with supercritical methanol:

A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes catalyst, and reduces catalyst effectiveness. The presence of water positively affected the formation of methyl esters in supercritical methanol method. Supercritical methanol is believed to solve the problems associated with the two-phase nature of normal methanol / oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. As a result, the reaction was found to be completed in a very short time. [18]

13.2. Synthesis of biodiesel via supercritical methyl acetate transesterification:

The use of methyl acetate instead of methanol for supercritical synthesis of glycerol-free biodiesel from vegetable oils is a new process where byproduct triacetin is formed. The production of triacetin is advantageous not only because it avoids that of glycerol but also because it was demonstrated that mixtures of FAME and triacetin obtained by this process are suitable as biodiesel fuel. The overall biodiesel production must then account not only for the FAME but also for the triacetin content. [14], [22], [24]

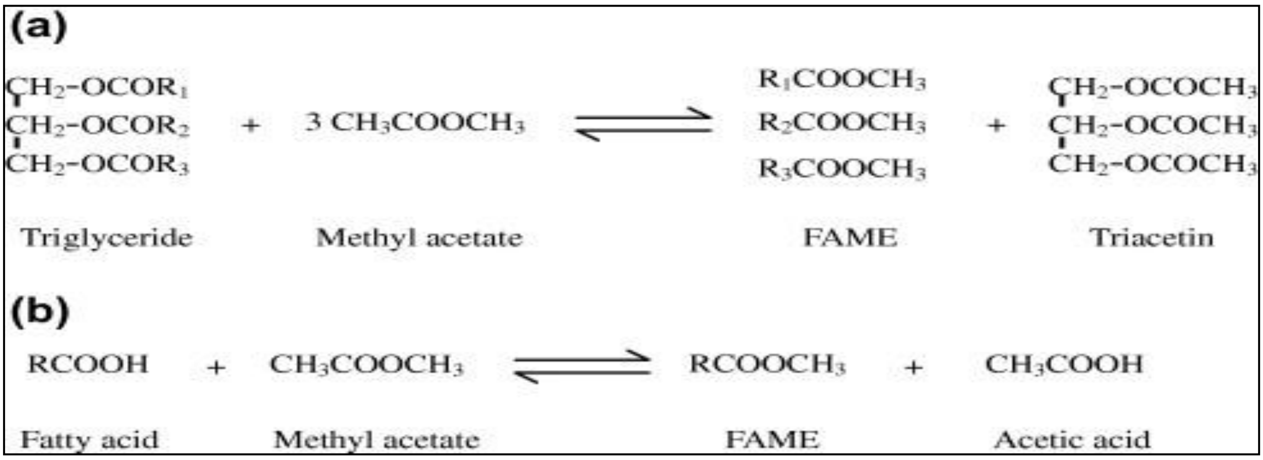


Fig 4 – biodiesel production with supercritical methyl acetate. [22]

13.3. Catalyst-free production of biodiesel using supercritical dimethyl carbonate :

Supercritical Dimethyl carbonate is used as a potential reactant for biodiesel production in this process, glycerol carbonate was produced as one of the byproducts. It is reported that this product has higher economic value than the abundantly available glycerol because it can be used as the raw materials for paint, dyes and adhesives and as a new source of new polymeric materials as well as a part of cosmetic composition and emulsifier.[14],[15] 13.4. Oscillatory flow reactor (OFR) for transesterification reaction. [06]

13.5. Ultrasound technology in transesterification reaction. [06]

13.6. Co-solvent [06]

14. Conclusion:

In recent years, biodiesel has become more attractive as an alternative fuel for diesel engines because of its environmental benefits and the fact that it is made from renewable resources. Currently, the alkali-catalyzed method is the most common and commercially available process for biodiesel production. However, water and free fatty acids (FFA) in oils / fats result in reducing the catalytic activity, thus, decreasing the yield and complicating the purification process. This prevented the use of waste vegetable oil as a reactant for biodiesel production which can reduce biodiesel production cost as compared to production from refined oil. Nevertheless, recent advances in technologies such as supercritical fluids, heterogeneous catalysts, and co-solvents have shown high potential in overcoming the limitations. But these are on a laboratory scale and if they go on industrial scale biodiesel production costs are reduced. Whereas on the other side petrodiesel is obtained from crude oil whose resources are depleting day by day. Because of this it is obvious that petrodiesel price will increase in the future. But because of the above techniques biodiesel cost may decrease in future & if this is possible, because of its environmental benefits and lower cost it will substitute petrodiesel to large extent. [02], [06]

15. Acknowledgement:

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16. References:

16.1. Satish L., *Biodiesel and Jatropha plantation*, India, Agrobios, May 2005, 1-4,10,30-32,38,56

16.2. Fukuda H. et al, ‘Biodiesel fuel production by transesterification of oils’, *Journal of bioscience and bioengineering*, **92**(5) (2001) 405-416.

16.3 Yusuf Chirsti, ‘Biodiesel from microalgae beats bioethanol’, *Trends in biotechnology*, **26**(3) (2008) 127-131.

16.4. Fukuda H., ‘Whole-cell biocatalysts for biodiesel fuel production’, *Trends in biotechnology*, **26**(12) (2008) 668-673.

16.5. Tianwani Tan at al, ‘Biodiesel production with immobilized lipase : A review' *Biotechnology advances*, **28** (2010) 628-634.

16.6. Lee et al, 'Homogenous, heterogenous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel : A review', *Biotechnology advances*, **28** (2010) 500-518.

16.7. Kale V., 'Biodiesel gaining popularity in India', *Inform*, **16**(7) (2005) 466-468.

16.8. Kale V.,' Jatropha - India's crop for biodiesel production', *Inform*, **16**(8) (2005) 532-533.

16.9. Ying Zang at al, 'Dissolution of waste plastics in biodiesel', *Polymer Engineering Science*, **50** (2010) 863-869.

16.10. Roberto Varse at al, 'Methyl ester biodiesel : opportunity or necessity?', *Inform*, **7**(8) (1996) 816-824.

16.11. Merlin P., 'Solutions for improved biodiesel', *Petroleum technology Quaterly*, **12** (2007) 7-8.

16.12. Mars A Dube at al, 'The use of biodiesel as a green polymerization solvent at elevated tempretures', *Polymer international*, **57** (2008) 854-862.

16.13. Gerhard Knothe, 'Biodiesel and vegetable oil fuels : Then & now' *Inform*, **17**(11) (2006) 729-731.

16.14. Jin – Suk Lee, 'Biodiesel production by heterogeneous catalysts and supercritical technologies' *Bioresource technology*, **101**(19) (2010) 7191-7200.

16.15. Shiro Saka**,** 'Dimethyl carbonate as potential reactant in non-catalytic biodiesel production by supercritical method', *Bioresource Technology*, **100**(5) (2009) 1793-1796.

16.16. Y. C. Sharma**, '**Advancements in development and characterization of biodiesel : A review, *Fuel*, **87**(12) (2008) 2355-2373.

16.17. Z. Helwani, 'Technologies for biodiesel production focusing on green catalytic techniques', *Fuel Processing Technology*, **90**(12) (2009) 1502-1514.

16.18. Dadan Kusdiana and Shiro Saka, 'Effects of water on biodiesel fuel production by supercritical methanol treatment' *Bioresourses Technology* ,**91**(3) (2004) 289-295.

16.19. A. Robles - Medina , 'Biocatalysis : Towards ever greener biodiesel production, *Biotechnology Advances*, **27**(4) (2009) 398-408.

16.20. L. Bournay, ' New heterogeneous process for biodiesel production : A way to improve the quality and the value of the crude glycerin produced by biodiesel plants' *Catalysis Today*, **106** (1/4) (2005) 190-192.

16.21. Avinash Kumar Agrawal , 'Biofuels (alcohol and biodiesel) applications as fuels for internal combustion engines', *Progress in Energy and Combution Science*, **33**(3) (2007) 233-271.

16.22. Pasquale Campanelli, 'Synthesis of biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification', *Fuel*, **89**(12) (2010) 3675-3682.

16.23. Rakesh Sarin, 'Jatropha–Palm biodiesel blends : An optimum mix for Asia', *Fuel*, **86**(10/11) (2007) 1365-1371.

16.24. Shiro Saka, 'A new process for catalyst-free production of biodiesel using supercritical methyl acetate' , *Fuel*, **88**(7) (2009) 1307-1313.

16.25. Melissa A. Hess, 'Attempts to reduce NO_X exhaust emissions by using reformulated biodiesel', *Fuel Processing Technology*, **88**(7) (2007) 693-699.