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Methanolysis of Cottonseed Oil for Biodiesel: As Renewable Source of Energy

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In present study, cottonseed oil is chemically standardized for biodiesel as renewable source of energy. Methyl ester (biodiesel) was produced by methanolysis of cottonseed oil with methanol in the presence of NaOH as catalyst. A maximum conversion of 90 % biodiesel was achieved by methanolysis of crude cottonseed oil at 60 ºC. The viscosity of pure biodiesel, B5, B10 and B20 were 5.102, 4.051, 4.090 and 4.082, respectively and are comparable with ASTM. Other properties of the cottonseed biodiesel such as specific gravity, cetane index, flash point, pour point and cloud point are close to the high speed diesel properties. Moreover, sulphur contents of the cottonseed biodiesel are much lower than high speed diesel.

Key Words: Methanolysis, Cottonseed oil, Biodiesel, Renewable energy.

INTRODUCTION

Pakistan is the fifth largest producer of cottonseed in the world, the third largest exporter of raw cottonseed, the fourth largest consumer of cottonseed and the largest exporter of cottonseed yarn. 1.3 Million farmers (out of a total of 5 million) cultivate cottonseed over 3 million hectares, covering 15 % of the cultivable area in the country. Cottonseed and cottonseed products contribute about 10 % to gross domestic product (GDP) and 55 % to the foreign exchange earnings of the country. Cottonseed production supports Pakistan's largest industrial sector, comprising some 400 textile mills, 7 million spindles, 27,000 looms in the mill sector (including 15,000 shuttle less looms), over 250,000 looms in the non-mill sector, 700 knitwear units, 4,000 garment units (with 200,000 sewing machines), 650 dyeing and finishing units (with finishing capacity of 1,150 million square meters per year), nearly 1,000 ginneries, 300 oil expellers and 15,000 to 20,000

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indigenous, small scale oil expellers (kohlus). It is by any measure Pakistan's most important economic sector. Not surprisingly, government policy has generally been used to maintain a stable and often relatively low domestic price of cottonseed, especially since 1996-2006 through the imposition of export duties, in order to support domestic industry.

Pakistan must face a new stage in the development of its oil industry. In account of the fluctuations in the oil industry, it is essential that the country extend its interest toward new sources of energy. A relatively new alternative that is currently booming worldwide is fuel obtained from renewable resources or biofuel. Since the cottonseed plant is commonly found in a cultivated state in many parts of the country its cultivation has a competitive advantage with respect to other oily yielding plants for biodiesel production.

Botanically cottonseed is *Gossypim hirsutum* belongs to the Malvaceae family and is commonly known as cottonseed plant and kapa. Annual sub-shrub, up to 1.5 m tall. Seeds contain approximately 46 % oil. Oil colouration ranges from a pale yellow to brown. It has a soft and faint odour and a highly unpleasant taste. Cottonseed oil dissolves easily in alcohol, ether, glacial acetic acid, chloroform, carbon disulfide and benzene[1,2]. Besides being used as a laxative, cottonseed oil is widely used in the industrial field because of its many properties. In the textile industry, cottonseed oil is used for moisturizing and removal of grease in fabrics and for the manufacturing of waterproof fabrics.

Considerable research has been done on vegetable oils as diesel fuel, such as palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil[3,4]. To date no report is available on the conversion of cottonseed oil to biodiesel. This study is therefore devoted to the conversion of cottonseed oil to biodiesel by methanolysis in the presence of a basic catalyst.

EXPERIMENTAL

Methanolysis of cottonseed oil to biodiesel was carried out by using methanol in the presence of sodium hydroxide as catalyst[5]. All chemicals used were of Merck chemicals, Germany. Cottonseed oil was supplied by Multan Agriculture Farm Multan and the biodiesel fuel was processed in biodiesel Lab. at Quaid-i-Azam University Islamabad Pakistan. The catalyst was dissolved into the alcohol by vigorous stirring in a small reactor. The oil was transferred into the reactor and then the catalyst/alcohol mixture was poured into the oil and the final mixture stirred vigorously for 2 h. Two phases were obtained at the end of the reaction: ester and crude glycerol. Biodiesel was observed in the top one and glycerin, a sub-product of the process, was observed in the lower one.

Fuel properties: Properties of biodiesel were tested according to ASTM biodiesel standards. Specific gravity at ASTM D-1298, flash point at ASTM

D-93, cetane index at ASTM D-976, pour point ºF at ASTM D-97, kinematic viscosity @ 40 ºC, sulphur contents (D-4294) and distillation at ASTM D-86 was determined for pure biodiesel B5, B10 and B20 in Quality Control Labs (QCL) at Attock Oil Refinery Ltd. Pakistan and are reported in Table-1.

Trials in engines: The performance trials for biodiesel and biodiesel mixtures were carried out at the test ground for internal combustion engines in the engine laboratory at Quaid-i-Azam University and also performed road engine test on the Toyota car (2-D) of Alternative Energy Development Board (AEDB).

RESULTS AND DISCUSSION

Biodiesel fuel is a medium length (C16 ± C18) chain of fatty acids and is comprised mainly of mono-alkyl fatty acid esters. Biodiesel fuel has the benefits of being non-toxic, biodegradable and essentially free of sulphur and carcinogenic ring components[6]. Feuge and Grose[7] highlighted the importance of using dry oils and a fatty acid content of less than 0.5 % by weight as biodiesel. A minimal content of water and free fatty acids in oil or fat is important for obtaining optimal results in the methanolysis (also known as transesterification) process. The existing water promotes the decomposition of esters in glycerol and fatty acids, which when combined with the fatty acids already free, saponify with the basic catalyst (soap formation) thus decreasing the efficiency of the methanolysis. A basic catalyst is used in the methanolysis of triglycerides with a low content of fatty acids. However, if the water and fatty acid contents are high, either an acid catalyst must be used or two methanolysis must be done, one with an acid catalyst and another with a basic one. Reaction rate increases with reaction time. In a performance trials with peanut, soy and sunflower oils at 60 °C using methanol and sodium methoxide as a catalyst and found that around 80 % of the conversion of esters occurs within the first few minutes of the reaction and after 1 h it reaches a range of about 90-96 %[8-10]. When an acid catalyst is used, reaction time can be much longer. The temperature of the methanolysis, its catalyst and quantity, the alcohol and its moral relation with the triglyceride depends on the oil or fat that is being used.

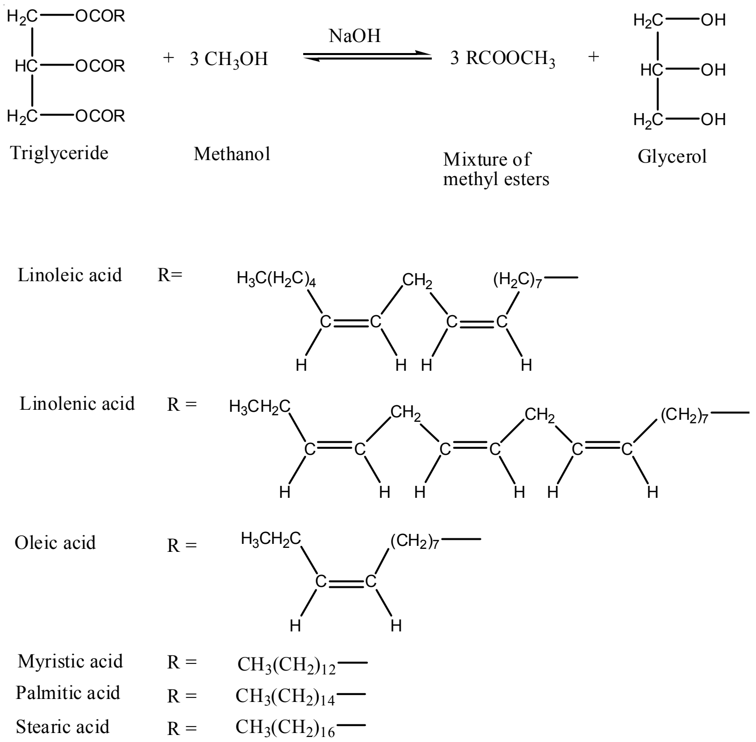
The efficiency in the process for the production of biodiesel from cotton-seed oil (which contains a mixture of linoleic, linolenic, myristic, oleic, palmitic and stearic fatty acids is shown in **Scheme-I**) was in the range of 85-90 %.

Table-1 shows a comparison between the properties of petroleum diesel and the boidiesel. It also presents data pertinent to the mixture of petroleum diesel and biodiesel in the following fashion: petroleum diesel (90 %)-biodiesel (10 %) : B10, Petroleum diesel (80 %)- biodiesel (20 %): B20.

TABLE-1
COMPARATIVE ANALYSIS OF COTTONSEED BIODIESEL PROPERTIES WITH HIGH SPEED DIESEL (HSD)

ASTM Method	Chemical properties	Cottonseed pure biodiesel	B5	B10	B20	HSD
ASTM D-1298	Specific Gravity @ 60/60 ºC	0.8708	0.8517	0.8542	0.8582	0.8502
ASTM D-93	Flash Point (PMCC) ºC	91.7	66	68	68	68
ASTM D-976	Cetane Index (calculated)	49.5	53	52	52	52.5
ASTM D-97	Pour point (ºC)	-3	0	0	0	0
	Colouration	1.0	2.0	1.5	1.5	2.0
ASTM D-4294	Sulphur contents	0.0073 %	0.5065 %	0.4789 %	0.4144 %	0.5430 %
ASTM D-445	Kinematic viscosity @ 40 ºC	5.102	4.051	4.090	4.082	4.34
ASTM D-86	Distillation					
	Distillation (IBP ºC)	305	225	175	177	167
	Distillation (10 % volume recovered at ºC)	326	255	230	232	235
	Distillation (20 % volume recovered at ºC)	328	270	260	262	250
	Distillation (30 % volume recovered at ºC)	330	285	275	277	265
	Distillation (40 % volume recovered at ºC)	332	300	290	292	280
	Distillation (50 % volume recovered at ºC)	334	315	305	308	295
	Distillation (60 % volume recovered at ºC)	336	330	320	322	310
	Distillation (70 % volume recovered at ºC)	338*	345	335	332	325
	Distillation (80 % volume recovered at ºC)	-	355	340	342	340
	Distillation (90 % volume recovered at ºC)	-	94	352	352	357
	Recovered vol. % @ 365 ºC	-		95	96	92

*Pungent fumes with green distillate.



Scheme-I

The performance of road run test revealed that engine ignited and operated normally with all the combustibles that were tested. Petroleum diesel presented the highest torque in all rpm values, even though the difference was very small when compared to the mixtures (B5, B10, B20) and pure biodiesel (B100). Power tests displayed a similar behaviour. When petroleum diesel was compared to the B5, B10, B20 and B100 mixtures, it was observed that B100 showed the highest combustible expenditure. This difference is possibly determined by the higher density of biodiesel since there will be a higher quantity of mass available to Petroleum diesel (0 %)- biodiesel (100 %): B100 Cottonseed Oil properties indicate a very low pour and cloud points which make this biofuel a good alternative in winter conditions, especially in cold areas.

The mixtures of 5 (B5), 10 (B10) and 20 (B20) per cent biodiesel-petroleum diesel showed good flow properties. It indicates that cottonseed oil biodiesel could be used as petroleum diesel additive improving both environmental and flow behaviour of the mineral fuel. React and release its energy for any given volume of injected combustible. For this reason, it is presumed that compensation in the difference of caloric power occurs, allowing for a negligible difference in torque and power when compared to petroleum diesel.

Although biodiesel has many environmental advantages it also has some performance drawbacks. In cold conditions the behaviour of the biofuels normally is even worse than that of petroleum diesel. At low temperatures biodiesel and diesel form wax crystals that can restrict the flow in a vehicle fuel system clogging fuel lines and filters. Cottonseed oil biodiesel exhibits different operation conditions. Due to low cloud point of cottonseed biodiesel, it is considered to be the good source of bio-energy in cold areas of Northern Pakistan. The methanolysis process of crude cottonseed oil was carried out by using NaOH as catalyst and methanol to form biodiesel. The conversion was 85-90 % at 60 ºC. The fuel properties of pure biodiesel and B5, B10 and B20 were matched with high speed diesel. These fuel properties were comparing well with accepted (ASTM) biodiesel standards. In the light of these experiments cottonseed oil is recommended as biodiesel source for commercialization and considered to be the cheapest source of energy at rural agricultural farm lands and cold areas in Pakistan. Therefore, on a large-scale process it would be less costly than chemical processes with other oils with a higher acidity level. Given the widespread presence and ease of cultivation of the cottonseed oil plant it could be used in crop substitution programs turning it into a factor that promotes growth in many regions affected by severe economic problems. The basification of cottonseed oil biodiesel is advisable taking into account that it is a renewable resource and because of its biodegradability and lower emissions it presents a favourable impact on the environment.

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