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Designer Biodiesel: Preparation of Biodiesel Blends by Mixing Several Vegetable Oils at Different Volumetric Ratios and their Corresponding Fuel Quality Enhancement

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Abstract

The fashion of production of biodiesel is emerging exponentially owing to greater disquiet about environmental protection and diminution of fossil fuel reservoirs. In this paper, a novel concept "Designer Biodiesel" for the biodiesel production has been accentuated. Since, the identical fatty acid composition of the biodiesel resembles to the precursor oil; therefore, its fuel properties are directly affected by the composition of the precursor oil. Various blends of some locally available vegetable oils such as Jatropha, Nahor, Yellow Oleander and Pongamia were prepared by mixing at different volumetric ratios (Yellow Oleander: Nahor); (Yellow Oleander: Jatropha); (Pongamia: Yellow Oleander), (Pongamia: Jatropha) and (Pongamia: Nahor). Biodiesel was prepared through a single step concentrated H_2SO_4 *catalyzed transesterification process in laboratory scale from the pure vegetable oils and selected blends and their fuel properties were analyzed according to the standard test methods.* ^1H *NMR technique has been used to determine fatty acid composition of the vegetable oils and the blends. The effect of fatty acid profile/composition on the properties of fuel like viscosity, cetane number, calorific value as well as iodine number had been detected.*

Keywords: Jatropha, pongamia, yellow oleander, nahor, oxidation stability.

Introduction

The thrust exerted by economical, political, social and environmental domain have hastened the investigation for alternative energy sources to minimize the utilization of fossil fuels. The increasing evidence of the potential impact of anthropogenic climate transformation through the expulsion of greenhouse gases CO_2 have moved the globe to entrust to declining these emissions through subsidies, taxes, and mandates[1] while consumers are gradually more demanding action from industry to shrink their effect on the atmosphere[2]. Out of these concerns, the large number of the globe's crude oil and natural gas reserves exists under unstable geopolitical region[3]. It has guided the exploration for economically feasible renewable a subject of national as well as fuel supply security. Eventually, there is limited fossil fuels preserved by nature and hence, substitutes must be set up before they get extinct which may turn out to the next century[4]. Biodiesel called fatty acid methyl ester (FAME) is a neat replenished fuel which can be applied in any Spark Ignited Direct Injection engine without the demand to redecorate the existing high techniques and has been obtained from familial feedstock. Biodiesel discloses superior bio deterioration than fossil fuels exceptional lubricant nature, non- toxic, less expulsion of carbon monoxide and insignificant sulfur content[5]. Most commonly, the biodiesel has been produced by the transesterification of animal fats, non-edible oils, dissipated cooking oil and edible oils etc. proffer a prospect to generate sustainable, renewable fuel, although advances must be made for it to be a viable competitor in the energy market[6]. Globally, 95 % of biodiesel production has been achieved from the edible oils which attain an effect on the universal difference to the market requirement and the delivery of foodstuffs in terms of large cost and the cutback of origin of food materials. Likewise, this is going to be a valid reason for the deforestation in several countries[7]. On the other hand, non-edible oils, which are not an indispensable part of an individual diet, must be increasingly utilized for the production of biodiesel. The plants of inedible vegetable oil generally has been grown in the soil appropriately for harvesting with much lesser charge compare to the price for edible vegetable oil plants. It has been reported that the overall fuel properties including oxidation stability, Cetane number, Calorific value etc have been robustly affected by the features of each of the fatty acid esters[8]. Hence, it has been proved that cetane number which is an ignition quality of a diesel fuel, declines with shortening in the length of the chain, an enhancement in branched moieties and rises in unsaturation in the chain of fatty acid[9]. Usually, when the cetane number is more it gives improved ignition quality but the saturated esters having large value of cetane numbers, acquire reduced cold-flow properties. Having lower melting points, unsaturated and polyunsaturated fatty esters are enviable for better low-temperature characteristics with less cetane numbers and lower oxidative stability and hence not suitable for diesel fuel. These kinds of problematic nature may be solved by the involvement of applying additives and altering the composition of fatty acid by means of both physical processes (winterization) and genetic adjustment which have guided to the development of notion of designer biodiesel with optimized fatty acid compositions for superior fuel properties. The chief idea to achieve biodiesel with constructive qualities is to have barely one chief part in a concentration as much as possible. The net fuel properties of the biodiesel have been determined by the features of the various individual fatty esters that comprise it. Thus, it has been uncovered that the features of the different fatty esters are resolved through the structural charateristics of the fatty acid and the hydroxy functionalities that consist of a fatty ester[10,11]. The purpose of this work is to prepare the model feedstock oils by blending of vegetable oils (Jatropha, Pongamia, Yellow oleander and Nahor) at different volumetric ratios in order to modify their fatty acid compositions. The current research makes an effort to examine the potential of the application of the blends fuel properties of biodiesel/methyl esters of model oils based on fatty acid compositions has also been determined and confirmed the results experimentally. In this paper, optimum blending ratio of the feedstock oils for the production of biodiesel with better fuel quality has also been achieved.

Material and Methods

Experimental: Methanol (extra pure), Petroleum Ether (40°-60 °C), H_2SO_4 (98% pure) and Na_2SO_4 (99% pure) have been procured from Merck India Ltd, Mumbai. All reagents were used without further purification. Various oil bearing seeds such as Yellow oleander (*Thevetia peruviana*), Nahor (*Mesua ferrea*), Karanja (*Pongamia pinnata*) and Jatropha (*Jatropha curcas*) were collected from different localities of Assam, India. Jatropha curcas and Pongamia pinnata seeds were supplied by Kaliabor Nursery, Nagaon (Assam), India.

The composition of the fatty acid of the vegetable oils and the blends were determined via ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). ^{1}H NMR spectra have been processed using "ACD NMR Processor Academic Edition"[12]. All ^{1}H NMR analyses were carried out at 25.5 °C with $CDCl_3$ and TMS as solvent and internal standard respectively. ^{1}H NMR spectra had been taken in a 400 MHz NMR spectrophotometer (JEOL, JNM ECS).

Extraction of oil: The seeds have been desiccated in daylight and further in an oven at 110 °C to remove any traces of moisture. The moisture free seeds were dehulled, kernels removed and grinded using a standard mixer grinder. Oil was extracted by the Soxhlet extraction technique using petroleum ether (40 °C-60 °C) as solvent[13]. The extracted oils were dried over anhydrous Na_2SO_4 and filtered to remove solid particles and impurities and stored in volumetric flasks.

Preparation of model oils (mixed oil feedstocks): Various blends were prepared by mixing Jatropha, Nahor, Yellow oleander, Karanja in different volumetric ratios. For preparing the model oils we mixed these oils in following volumetric ratios. Yellow Oleander:Nahor (1:1 to 1:8 and 2:3); Yellow Oleander:Jatropha (1:1 to 1:3, 2:3 and 2:4); Pongamia: Yellow Oleander (2:1), Pongamia:Jatropha (1:1) and Pongamia: Nahor (6:1).The fatty acid compositions of these model feedstocks were evaluated and fuel properties of their corresponding methyl esters were predicted based on empirical relations. Some fuel properties such as oxidation stability, iodine number, acid value, calorific value and kinematic viscosity of biodiesel from the mixed feedstocks were determined and compared with the predicted values. These blends were prepared on the basis of their fatty acid composition so as to improve the fuel quality of the corresponding biodiesel.

A general procedure for biodiesel production by blending several oils: In 100 mL round bottom flask, different oils to be blended were added in different volumetric ratios. In another flask 6 equivalents of methanol with respect to the oils to be blended and 2 wt% of H_2SO_4 were mixed. Then the contents in second flask were added drop wise to the first one at 70°C for six hours. The mixture was stirred continuously till the reaction completed. Then the contents of the reaction was moved to separating funnel and allowed to settle. The two layers were then taken apart, upper layer was biodiesel and lower part included glycerine. Excess methanol is separated from the mixture using rotary vacuum evaporator. Upper part (biodiesel) was provided washing with distilled water several times to neutralize the excessive acid along with the removal of glycerin. Finally biodiesel is dried over anhydrous $NaSO_4$ and characterized through ^{1}H NMR technique.

Results and Discussion

Fatty acid profiles/compositions of feed stocks: The table below shows the fatty acid compositions of single and model oil feedstocks (created by blending) evaluated using^1 H NMR spectroscopy.

Comparison of Experimental and Predicted Properties of biodiesel: All the predicted and experimental results of cetane number, calorific value, kinematic viscosity, iodine number and oxidation stability that we obtained, have been presented in table-2.

It is found that the predicted values which we calculated are nearly equivalent to those obtained experimentally. Thus, it is clear that the method we used is the correct one and can be successfully applied for the determination of fuel properties of biodiesel. It is seen from table-2 that cetane number, kinematic viscosity and oxidation stability increase with the increase in saturation. But unlike these properties, iodine value and density decrease with the increasing degree of saturation. Calorific value increases with increasing chain length.

Table-3 lists the experimental values of some important fuel properties such as density, IV, viscosity, calorific value, OSI, cloud point and pour point of the prepared samples. Overall the trends for variation of fuel properties were found to be similar to the empirical results presented in table 2. Additionally, all the characteristics of the biodiesel obtained from the feedstocks were in accordance with the standard specifications (ASTM D6751 and EN 14214).

The effect of blending ration on various properties has been portrayed in figure 1. As per the ASTM 6751 standard, the cetane number for biodiesel should be in the range of 48-65 which has been achieved by all the blended samples in our study [figure 1 (a)]. Accordingly the calorific value [figure-1(b)] meets the same requirement. The total unsaturation of a fatty acid material has been measured by IV in g iodine/100 g of a sample when iodine is added properly to the double bonds. An additional notion making use of the IV is that it signifies the tendency of the oil or fat to polymerize and produce engine dumps. Hence, in our study [figure 1 (c)] the IV for K+N (1:1) corresponds to the lower value amongst others which is suitable for the performance of an engine. The matter of oxidation stability influences biodiesel mainly during long period of preservation. As presented in the figure 1 (d), the value for oxidation stability is recorded the highest in case of K+N (1:1) blend and therefore, appropriate for the storage.

Table-1
Fatty acid composition of single and model oil feedstocks

Sample's name	**Fatty acid profile/composition (wt %)**				
	Linolenic (C18:3)	**Linoleic (C18:2)**	**Oleic (C18:1)**	**Total Saturated**	**OSI (h)**
J (Jatropha)	0.5	37.99	52.51	9	4
K (Karabi)	1.78	23.81	56.66	17.75	6.07
N (Nahor)	3.43	13.21	65.45	18.2	6.25
P(karanja)	4.51	22.22	51.8	21.47	5.77
K+N (1:1)	3.5	15.52	62.67	18.31	13.4
K+N (2:3)	3.87	14.07	57.74	24.32	7.57
K+N (1:2)	3.68	14.65	62.68	19.01	6.4
K+N (1:3)	3.56	14.81	57.61	24.02	7.51
K+N (1:8)	5.21	9.53	66.67	18.59	6.41
K+J (1:1)	1.29	18.69	64.1	15.92	2.65
K+J (2:3)	1.33	30.53	50.66	17.48	5.89
K+J (1:2)	0.8	32.32	52.19	14.69	5.28
K+J (1:3)	4.9	21.73	56.05	17.32	5.92
K+J (2:4)	1.05	29.42	52.19	17.34	5.89
P+K (2:1)	3.49	18.51	53.11	24.89	7.62
P+J (1:1)	2.51	26.56	51.01	19.92	6.45
P+N (6:1)	4.54	20.35	45.84	23.27	7.05

The used symbols represent: J = Jatropha (*Jatropha curcas*) ; N = Nahor (*Mesua ferrea Lin.*)*;* K = Karabi or yellow oleander (*Thevetia peruviana*); and P = Karanja (*Pongamia pinnata)*

Table-2
Comparison of Predicted and Experimental biodiesel fuel properties

	Cetane number CN	**Calorific value (KJ/g) CV**		**Kinematic viscosity (cSt) ν**		**Iodine value (IV) (mg I_2 g^{-1})**		**OSI (h)**	
Sample Code	**X**	**X**	**Y**	**X**	**Y**	**X**	**Y**	**X**	**Y**
J	52.26	39.66	40.49	4.27	5.05	110.95	109.00	4.00	2.0
K	57.03	39.78	39.79	4.33	5.11	94.25	90.00	6.07	5.82
N	60.95	39.91	39.75	4.61	6.17	88.16	72.54	6.25	3.87
P	57.89	39.76	40.20	4.30	3.12	94.43	84.33	5.77	3.79
K+N (1:1)	59.32	39.85	39.12	4.61	4.5	89.58	80.34	13.4	14.12
K+N (2:3)	61.41	39.86	38.91	4.5	4.42	83.83	83.43	7.57	8.21
K+N (1:2)	60.58	34.79	34.33	4.5	4.32	88.54	89.21	6.4	6.5
K+N (1:3)	61.75	39.88	38.84	4.57	5.54	84.18	83.23	7.51	7.43
K+N (1:8)	61.25	39.9	37.11	4.6	5.71	87.13	85.21	6.41	6.31
K+J (1:1)	57.61	38.73	37.23	4.26	5.3	90.52	93.34	2.65	2.23
K+J (2:3)	57.01	39.65	39.53	4.29	4.32	99.5	98.42	5.89	6.4
K+J (1:2)	56.51	39.77	40.10	4.29	5.43	102.54	100.43	5.28	5.54
K+J (1:3)	58.8	39.77	39.32	4.31	6.11	98.23	86.21	5.92	5.74
K+J (2:4)	57.33	39.77	38.75	4.3	4.31	98.19	97.55	5.89	6.63
P+K (2:1)	59.49	39.76	39.42	4.34	4.44	86.52	86.34	7.62	7.85
P+J (1:1)	57.63	39.78	36.53	4.3	4.82	96.06	95.58	6.45	7.21
P+N (6:1)	55.05	39.55	40.5	4.28	5.21	86.21	85.67	7.05	6.89

X= Predicted Y= Experimental

Table-3
Experimental determination of fuel properties of prepared samples

Samples name	**Density @ 15 °C g/c.c**	**Viscosity @ 40 °C (cSt)**	**Calorific Value (KJ/g)**	**Iodine value (mg$I_2$$g^{-1}$)**	**OSI (h)**	**Cloud point (°C)**	**Pour point (°C)**
J	0.878	5.05	40.49	109	2.00	9	-3
K	0.882	5.11	39.79	90	5.82	6	-8
N	0.891	6.17	39.75	72.54	3.87	7	3
P	0.884	3.12	40.2	84.33	3.79	15	6
K+N (1:1)	0.867	4.35	38.53	80.34	13.4	8	5
K+N (2:3)	0.872	4.34	38.60	46.83	11.78	0	-5
K+N (1:2)	0.887	4.85	38.73	54.385	10.6	10	-2
K+N (1:3)	0.891	4.97	38.88	49.66	7.98	9	-3
K+N (1:8)	0.895	5.0	38.98	69.52	6.73	-	-
K+J (1:1)	0.877	4.24	38.42	51.65	11.45	4	2
K+J (2:3)	0.889	4.41	38.53	43.466	13.01	9	5
K+J (1:2)	0.890	4.59	38.58	55.14	12.48	12	8
K+J (1:3)	0.893	6.0	38.79	60.12	10.11	16	10
K+J (2:4)	0.810	4.19	38.62	55.506	10.51	12	7
P+K (2:1)	0.887	3.96	38.98	59.36	9.06	19	9
P+J (1:1)	0.897	5.41	38.47	53.01	8.27	5	1
P+N(6:1)	0.875	5.21	37.52	54.11	8.43	11	3

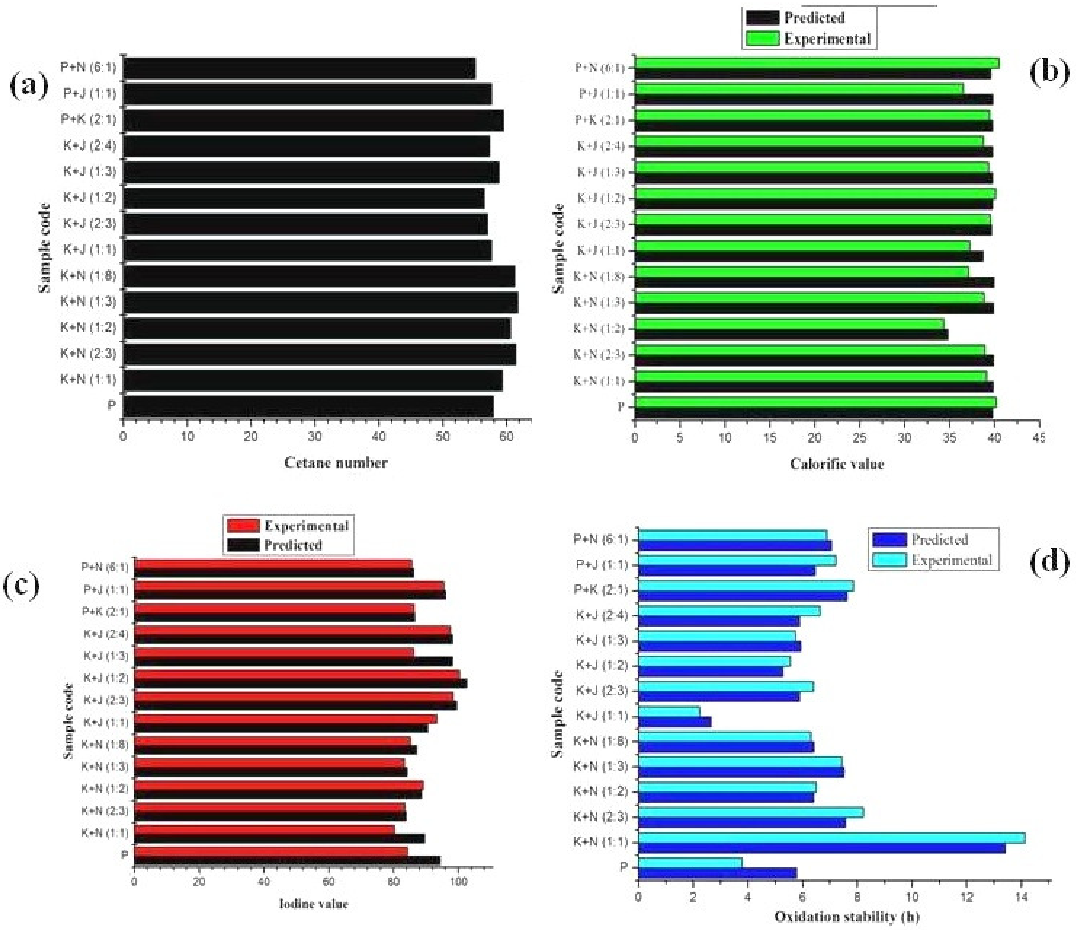

Figure-1
Effect of blending ratio on (a) Cetane number, (b) Calorific value, (c) Iodine value and (d) Oxidatioin stability of prepared biodiesel samples

Conclusions

In conclusion, we have an improved fuel quality of biodiesel from locally available four non-edible vegetable oils by modifying their fatty acid/ester composition via blending in different volumetric ratios. The determination and measurement of several physical and fuel properties of the biodiesel blends demonstrated the outcomes within the permissible limit for B100 along the boundary of specification of ASTM standard. The blends at various ratios may be applicable as a raw material for the production of biodiesel but among them yellow oleander: nahor (1:1 volumetric ratio) has shown advancement in better fuel quality. Moreover, blending of different vegetable oils has helped in enhancing the total feedstock amount. The availability of feedstock varies from one region to another and if we depend on a single feedstock then it will not be possible to meet the optimum production of biodiesel as requirement. Thus, this work has corroborated an advantageous idea of blending in terms of fuel quality as well as feedstock amount enhancement and is going to be a breakthrough in domain of industry and human civilization.

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