

Prospects of castor (*Ricinus Communis* L.) genotypes for biodiesel production

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Received : 31 December, 2012

ABSTRACT

The search of suitable non-edible crop for biodiesel production has led to exploration of potential of castor for biodiesel production. India ranked topmost in the castor oil production in world. Six hybrid genotypes and one variety of castor were studied for the suitability for biodiesel. The seed characteristics, oil characteristics and fatty acid profile were evaluated under the study. The value of biodiesel traits were then computed. The ricinolic acid varied from 84.30-87.80 %. Under the present study the ricinolic acid content was significantly negatively correlated with palmitic fatty acid ($r=-0.953^{**}$); stearic fatty acid ($r=-0.809^{*}$); oleic fatty acid ($r=-0.811^{**}$) and linoleic fatty acid ($r=-0.891^{**}$). The oil stability index (O/L ratio) and O/R ratio (for oxidative stability) were also computed. In the present study, the castor genotypes evaluated have met the specification of Cetane number (CN) (<65) and Iodine value (IV) (<115) of biodiesel standards.

Key Words: Castor genotypes, biodiesel, ricinolic acid, fatty acid, cetane number

The depleting reserves of fossil fuel and increasing demand for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative sources of energy, which can supplement or replace fossil fuels. About one hundred years ago, Rudolf Diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893. Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Support policies by governments in different countries like Europe, Brazil, Namibia and India gave a boost to the use of

biodiesel fuels for transport like the EU Directive 2003/30/EC in Europe. The National Mission on Biofuels in India targeted to achieve 20% blending of biodiesel (B20) by 2012. The mission aimed at bringing 4,00,000 ha of marginal land under cultivation of non-edible oilseed crops mainly *Jatropha*. However, castor is a viable alternative to *Jatropha* due to its shorter growing period and standard agronomic practices for assuring good yields.

Castor (*Ricinus communis* L) belongs to Euphorbiaceae family grown over a wide range of geographical regions in tropical as well as warm temperate regions of the world. India with a production of over 1.35 MT castor seeds plays a monopolistic role in castor production in world (Anonymous, 2012). Gujarat is key in the castor production in India. Castor oil, pale amber viscous liquid derived from the seeds. Castor oil is non edible but very important industrial oil which is

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characterized by its high viscosity, specific gravity and acetyl value. Ricinolic acid (12-hydroxy-9-octadecenoic acid) is the principal component of castor oil, which occurs upto the extent of 90-95 % of the total fatty acid and is responsible for the high viscosity and other peculiar characteristic of oil. Ricinolic acid allowing castor oil to be miscible with methanol and ethanol at 30 °C and facilitates transesterification without heating and lowers the cost of production. Though, castor oil is about 100 times as viscous as diesel fuel but transesterification significantly reduces the viscosity. Oil content in castor seed varies from 47 to 49% (Weiss, 2000) which is much higher than the values reported for *Jatropha* (Ravindrababu *et al.*, 2006).

This is an excellent option for biodiesel production in India since sufficient castor seed to the tune of 850 thousand tonnes is available in the country (Damodaram and Hegde, 2007). The fatty acids, being biological in origin, composition is affected by the genetic as well as edaphological characteristics (Abolfazi Alirezalu *et al.*, 2011). Gujarat state has released six castor hybrids so far, which are having yield potential of 3000 kg/ha seed yield under irrigated condition accentuates the need to explore the potential of castor as a biodiesel crop using pure castor methyl esters (B100) or its blend with petrodiesel in different volume ratios (B10 or B20) (Pathak, 2009). The information on suitability of castor genotypes for biodiesel production and correlation with quality aspects has not been generated until now and is highly essential for breeding and selection of efficient biodiesel cultivars. With this objective, all 6 released castor hybrids and one genotype GAUC-1 were evaluated

for their fatty acid profile and the biodiesel related traits like saponification number, iodine value and cetane number.

MATERIALS AND METHODS

Six released castor hybrids and one variety were selected for the study were selected for the present study. The castor crop was grown in the irrigated conditions at Entisols of the Main Castor Mustard Research Station, S.D.A.U., Sardarkrushinagar, Gujarat (Table 1). Standard agronomic practices were practiced for raising the crop. The seeds were harvest at physiological maturity and analysed for seed physical properties viz. 100 seed weight (g), seed oil content (%), kernel oil content (%), kernel (%), seed coat (%). The castor seed oil was extracted as per method prescribed (4-38 on soxhlet apparatus, AOCS, 1951). The oil quality parameters like viscosity was determined on viscometer (A&N Vibro Viscometer, Model SV 10) and the colour value was determined on Levibond tintometer with one inch cell. The other oil quality parameters like specific gravity and refractive index were determined as per standard methods. The fatty acid profile was determined on FTNIR (Bruker Optics-IFS MPA System) as per standard methods. All this physical parameters of seed, oil quality as well as the fatty acid profile under study are very useful for industrial purposes. Saponification number (SN) and iodine value (IV) of oils were calculated as per standard methods. Cetane number (CN) was calculated from Eq. $CN=46.3+5458/SN-0.225*IV$. Oleic and linoleic acids (O/L) ratio and Oleic and ricinolic acids (O/R) ratio were computed. Correlation coefficient was worked out for the various character studied.

Table 1 Castor genotypes evaluated for seed and seed oil quality characteristics

Genotype	Variety / Hybrid	Year of release	Productivity (kg/ha)
GAUC 1	Variety	1973	1242
GAUCH 1	Hybrid	1973	1518
GCH 2	Hybrid	1985	1747
GCH 4	Hybrid	1986	1985
GCH 5	Hybrid	1994	2826
GCH 6	Hybrid	1999	2325
GCH 7	Hybrid	2006	3000

RESULTS AND DISCUSSION

Seed quality parameters

Seed and oil yields are the most important traits which will decide the future of castor as an energy crop. The data of seed quality parameters of castor genotypes studied were presented in Table 2. The highest test wt (37.1g) was recorded in GCH 5 while lowest in GAUC 1 (17.1g). Seed weight is considered as the most important characteristics for milling. Maximum recorded value of seed oil content was at par for the hybrids GCH 4, GCH 5 and GCH 6 ($49.7 \pm 0.2\%$) while the hybrid GAUCH 1 recorded the minimum seed oil content (48.6%). Reviewing available literatures, 292 kg/ha was the maximum initial seed yield among *Jatropha* progenies evaluated for the selection of high yielding genotypes (Rao *et al.*, 2008) while oil yield up to 95 kg/ha is expected considering an average of 32.5% oil content which is significantly low compared to castor yields. The kernel oil content was varied from 57.7 to 59.9 per cent. GCH 2 recorded the maximum kernel oil (59.9%). The value of kernel (%) was varied from 69.4 (GCH 7) to 72.4 (GCH 5). The kernel (%) were highly significantly correlated with seed coat (%) ($r = -0.997^{**}$). Lower value of seed coat (%) is desirable character for better oil recover (Moskin, 1986).

Oil quality parameters

The specific gravity was varied within a very narrow range under present study (0.960 to 0.962). The value of specific gravity has positive correlation with test wt ($r = 0.835^*$). In general, the oil from castor hybrids were more viscous than the variety (GAUC 1), which recorded the minimum viscosity (584 centipoise). The castor hybrid GCH 4 recorded the maximum viscosity (678 centipoise). The viscosity showed positive correlation with test wt. ($r = 0.791^*$) and seed oil (%) ($r = 0.764^*$). The hydroxy group of ricinolic acid imparts a very high degree of viscosity and oxidative stability which was four times more stable than the olive oil (Patel *et al.*, 2004). Among the castor genotypes, refractive index varied from 1.4773 to 1.4788. The values of specific gravity were in line with the findings of Abitogun *et al.* (2009). The value of refractive index is an indication of the level of saturation of the oil.

Fatty acid profile

The quality of oil is a function of its fatty acid composition (Table 3). The value of free fatty acid as oleic acid is varied from 1.93 % (GCH 6) to 7.03 % (GCH 2). However, the oil of high value of free fatty acid could be modified by subjecting it to refining and this would also improve its quality for industrial usage. This could be used to check the level of oxidative deterioration of the oil by enzymatic or chemical oxidation. The fire, flash and smoke points of the oil has linear relationship with the content of the free fatty acid present in the oil (AOAC, 1990). A good quality castor oil should have the acid value within the range of 3-4 (Kulkarni and Ramanamurthy, 1977). Expelled castor oil has generally of low fatty acidity (<3) while solvent extracted oils has higher acid value than the required standard. Saturated fatty acids, palmitic and stearic acids were in the range of 1.11–1.58% and 1.26–1.70%, respectively. The present study indicated significant positive correlation among saturated fatty acids, palmitic and stearic acids ($r = 0.790^*$). Mono unsaturated fatty acid- oleic acid varied from 4.16 (GCH 4) to 5.40 % (GAUCH 1). Higher value of oleic acid is a desirable trait for high oxidative stability, hence suitability of castor oil for bio-diesel production (Rojas *et al.*, 2004). However, the oleic acid is much lower than vegetable oils like peanut (53%), rapeseed (33%), soybean (24.9%) and sunflower (25%) (Ramos *et al.*, 2009). The poly unsaturated fatty acid like linoleic and linolenic fatty acid were in the range of 4.98 to 6.09 and 0.70 to 1.13, respectively. The maximum value of both the fatty acids were found in hybrid GCH 5. Linoleic fatty acids was significantly positively correlated with palmitic fatty acid ($r = 0.969^{**}$) and stearic fatty acid ($r = 0.765^*$) under the study.

Ricinoleic acid, the predominant monounsaturated fatty acid varied among castor genotypes from 84.3 (GAUCH 1) to 87.8 % (GCH 4). The functional group causes ricinoleic acid to be unusually polar and also allows chemical derivatization that is not practically possible with most other vegetable oils. Under the present study the ricinolic acid content was significantly negatively correlated with palmitic fatty acid ($r = -0.953^{**}$); stearic fatty acid ($r = -0.809^*$); oleic

Table 2 Determination of seed quality characteristics of released castor hybrids/varieties

Genotypes	Test wt. (gm)	Seed oil content (%)	Kernel oil content (%)	Kernel (%)	Seed coat (%)	Specific gravity (g/Cc) at 25°C	Refractive Index (nd) at 25°C	Viscosity (cp) at 25°C
GAUCH 1	25.9	48.6	59.0	70.8	29.2	0.960	1.4778	584
GCH 2	24.7	49.8	59.9	70.6	29.4	0.960	1.4780	621
GCH 4	32.2	49.7	59.2	71.6	28.2	0.961	1.4783	678
GCH 5	37.1	49.8	59.0	72.4	27.6	0.962	1.4780	656
GCH 6	31.3	49.9	59.3	70.7	29.3	0.962	1.4778	632
GCH 7	29.9	49.6	58.3	69.4	30.6	0.961	1.4881	635
GAUC 1	17.1	49.1	57.7	70.6	29.4	0.960	1.4773	589
Mean	28.3	49.5	58.9	70.9	29.1	0.961	1.479	627.9
SEm±	2.4	0.2	0.3	0.4	0.4	0.000	0.001	12.8
SD	6.4	0.5	0.7	0.9	1.0	0.001	0.004	33.8
Range	17.1-37.1	48.6-49.9	57.7-59.9	69.4-72.4	27.6-30.6	0.960-0.962	1.477-1.488	584-678

Table 3 Fatty acid composition of castor hybrids/varieties

Genotypes	% free fatty acid as Oleic acid	Fatty acid composition (%)					
		C16:0 Palmitic	C18:0 Stearic	C18:1 Oleic	C18:2 Linoleic	C18:3 Linolenic	C18:1 (OH) Ricinoleic
GAUCH 1	2.49	1.58	1.70	5.40	5.88	1.11	84.3
GCH 2	7.03	1.53	1.47	5.35	6.05	0.82	84.8
GCH 4	1.97	1.11	1.26	4.16	4.98	0.70	87.8
GCH 5	1.95	1.56	1.63	4.64	6.09	1.13	85.0
GCH 6	1.93	1.18	1.44	4.96	5.10	0.98	86.3
GCH 7	2.50	1.26	1.27	4.82	5.24	0.82	86.6
GAUC 1	2.49	1.28	1.54	4.28	5.51	0.78	86.6
Mean	2.9	1.36	1.47	4.80	5.55	0.91	85.91
SEm±	0.7	0.07	0.06	0.18	0.17	0.06	0.47
SD	1.8	0.20	0.17	0.48	0.46	0.17	1.25
Range	1.93-7.03	1.11-1.58	1.26-1.70	4.16-5.40	4.98-6.09	0.70-1.13	84.30-87.80

fatty acid ($r=-0.811^{**}$) and linoleic fatty acid ($r=-0.891^{**}$). The fatty acid profile was resembling with the findings of Lakshminarayana *et al.* (1984).

Oil stability index

Oleic/linoleic acid (O/L) ratio, also known as oil stability index varied from 0.76 (GCH 5) to 0.97 (GCH 6) in the present study. High O/L ratio indicated higher stability. The presence of antioxidants is higher in cold extracted oils than solvent extracted or pure methyl esters. The CaME prepared from cold extracted castor oil with high natural antioxidants is less prone to auto-oxidation (Berman *et al.*, 2011). The values are in corobation with the findings of Lavanya *et al.* (2012).

Oleic/ricinoleic acid (O/R) ratio

The oleic/ricinoleic acid ratio (O/R) among the genotypes varied from 0.047 (GCH 4) to 0.064 (GAUCH 1). High oleic and low ricinoleic acid contents in castor oil could have industrial uses requiring high oxidative stability such as biofuel applications requiring lower ricinoleic levels than the standard castor oil (Rajos *et al.*, 2004). The value of O/R has highly significant positive correlation ($r=0.997^{**}$) with oleic fatty acid but negative correlation with ricinolic acid ($r=-0.848^{*}$).

Biodiesel traits

Saponification number (SN) and Iodine Value (IV) depend on the molecular weight, percentage concentration of unsaturated fatty acid components and the number of double bonds in the fatty acids. This is used to establish the suitability of the genotypes for their use as biodiesel which can meet the specification of biodiesel standards of USA, Germany and Europe. The biodiesel traits are presented in Table 4.

Cetane number

Cetane number (CN), a widely used diesel quality parameter is related to the ignition delay time and combustion quality. The SN was minimum in the hybrid GCH 6 and maximum in GCH 2 while the IV was varied from 75.9 (GAUC 1) to 83.6 (GCH 7). The higher value of IV was noticed in GCH5 and GCH 6 also. However, the CN values were lowest in GCH 5

(58.0) and highest in GAUC 1 (59.6). These ranges are in corroboration with international specifications (Scholz and Da Silva J, 2008). The CN is a relative measure of the interval between the beginning of injection and auto-ignition of the fuel. Higher the CN, faster the engine with a shorter interval between injection and ignition and the greater its combustibility and ignition properties (Ramos *et al.*, 2009). Fuels with low CNs will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate better on fuels with CNs above 50. The CN of the majority of biodiesel fuels is actually higher than petrol or diesel, and the CN of castor oil biodiesel is in a good range for diesel engines. This is one of the important parameters, which is considered during the selection of Fatty acid methyl esters (FAMES) for use as biodiesel. As per the specifications given in biodiesel standards, the cetane number needs to be a minimum of 49 in Germany (DIN V 51606) or 51 in Europe (EN 14214) which is applicable to FAME or 47 as per the American Society for Testing and Materials (ASTM) D6751 applicable to FFAE (American Society for Testing Materials, 2002).

Iodine value

Iodine value indicates the total unsaturation within a mixture of fatty acid and expressed in grams of iodine which react with 100 g of the sample by adding iodine to the double bonds. The presence of unsaturated fatty acid component in FAMES is required up to an extent, as it restricts the FAMES from solidification. However, with higher degree of unsaturation, FAMES are not suitable for biodiesel as the unsaturated molecules react with atmospheric oxygen and are converted to peroxide. Cross-linking at the unsaturation site can occur and the material may get polymerized into a plastic-like body. In an internal combustion engine where high temperature is very common, the polymerization process can get accelerated and the engine can quickly become gummed up with the polymerized FAMES leading to the formation of deposits or deterioration of the lubricating quality. To avoid this situation, biodiesel standards have set a minimum limit of IV in their specifications (Ramos *et al.*, 2009). Iodine value is limited to 120 g I₂/100 g in the

European biodiesel standard. In the present study, all the seven castor genotypes, which qualify the specification of CN, also meet the specification of IV. All of them have IV less than 115, the lowest maximum limit among the three biodiesel standards. Besides, the concentration of linolenic acid and acid containing four double bonds in FAMES should not exceed the limit of 12% and 1%, respectively (Mittelbach, 1996). None of the castor cultivars' FAMES contain fatty acid with four double bonds. Generally, FAMES with higher CN are ideal for biodiesel purpose. However, with increase of CN, IV decreases which means degree of unsaturation decreases. This situation will lead to the solidification of FAMES at higher temperature. To avoid this situation, the minimum limit of CN (47) has been specified in US biodiesel standard (American Society for Testing Materials, 2002). In the present study, castor genotypes evaluated have already met the specification of CN (<65) and IV (<115) of biodiesel standards. Correlation studies between fatty acid profile and biodiesel traits in the present study indicated that free fatty acid as oleic acid had a significant and positive correlation with SN

($r = 0.845^*$); IV had a significant and positive correlation with specific gravity ($r = 0.905^{**}$) and test weight ($r=0.809^*$). The CN value has positive correlation with specific gravity ($r=0.862^*$) but negatively with test weight ($r=-0.818$).

CONCLUSION

India is the leading country in world for the castor seeds production. The Six hybrid genotypes and one variety of castor were studied for the suitability for biodiesel. On the basis of cetane number all the genotypes hybrid castor and variety were found promising for biodiesel as they complied with the major specification of biodiesel standards of USA, Germany and Europe. High O/L ratio of the genotypes studied indicated higher oil stability. High oleic and low ricinoleic acid contents in castor oil could have industrial uses requiring high oxidative stability such as biofuel applications requiring lower ricinoleic levels than the standard castor oil. GCH-7 variety is most suitable for biodiesel production due to higher seed yield.

Table 4 Biodiesel traits for castor genotypes

Genotypes	Oleic / linoleic	Oleic / ricinolic	Saponification number		
			(mg KOH/g oil)	Iodine value (I_2 /100 g)	Cetene number
GAUCH 1	0.92	0.064	180.2	77.4	59.2
GCH 2	0.88	0.063	182.2	76.3	59.1
GCH 4	0.84	0.047	180.6	79.8	58.6
GCH 5	0.76	0.055	179.4	83.1	58.0
GCH 6	0.97	0.058	178.6	83.5	58.1
GCH 7	0.92	0.056	179.5	83.6	59.4
GAUC 1	0.78	0.049	179.8	75.9	59.6
Mean	0.87	0.1	180.0	79.9	58.9
SEm±	0.03	0.0	0.4	1.3	0.2
SD	0.08	0.0	1.1	3.5	0.6
Range	0.76-0.97	0.047-0.064	178.6-182.2	75.9-83.6	58.0-59.6

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