

Full Length Research Paper

Production of both esters and biogas from Mexican poppy

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This paper details a dynamic evaluation of a procedure for extracting both, ester and biogas from seeds and waste of Mexican poppy (*Argemone mexicana*) using simple and inexpensive technique. Results showed that *A. mexicana* seed contains 30% oil. Through the process of transestrification, oil extracted from seed, has been converted to its ester. Methanol gives good separation of ester with *A. mexicana* compared to ethanol and *A. mexicana* methyl ester showed closer physical property to diesel. Calorific value of seed waste was 4621 Kcal/Kg and C/N ratio was 11. The experiment for biogas production was accomplished in two conditions viz sunlight (22- 30°C) and at room temperature (16-20°C) for 33 days. Sunlight increase ten times biogas production compared to room temperature. Biogas produced through anaerobic digestion of seed waste contained 52% methane. This process is suitable for small-scale industries and agricultural farms.

Key words: Transestrification, energy conservation, anaerobic digestion, methane, biogas, methyl ester.

INTRODUCTION

For advancement of civilization and socioeconomic developmental progress, the world is dependent on various energy resources like petrochemicals, coal, natural gas, hydro and nuclear electric powers. Further, our energy requirements increase with the enhancement in the energy demand of increasing world human population. However, these sources are finite and at current usage rates will be consumed shortly (Srivastava and Prasad, 2000). An alternative renewable and sustainable fuel must be need for the time and should be technically feasible, economical eco-friendly and readily available (Meher et al., 2006). Biogas and esters from vegetable oils are two alternative sources of energy, which are renewable as well eco-friendly. Oil esters represent an alternative to fossil fuel. To produce these esters, use oils of plant origin like vegetable oils and tree born oil seeds are used. Methyl esters of fatty acids are produced by the transesterification of triglycerides of vegetable oils with methanol with the help of a catalyst (Klass, 1998). These fuels are biodegradable and have

low emission profiles as compared to petroleum diesel. Usage of ester will allow a balance to be sought between agriculture, economic development and the environment. On the other hand, biogas technology offers a very attractive route to utilize certain categories of biomass meeting partial energy needs. In fact proper functioning of biogas system can provide multiple benefits to the users and the community resulting in resources conservation and environmental protection (Yadvika et al., 2004). It is the product of anaerobic degradation of organic substrates carried out by a consortium of microorganisms and depends on the various factors such as pH, temperature, hydraulic retention time, C/N ratio. Anaerobic digestion is a complex, natural, multistage process of degradation of organic compounds through a variety of intermediates into methane and carbon dioxide, by the action of a consortium of microorganism (Gujer and Zehnder, 1983). The genus *Argemone* (Papaveraceae) comprises almost 30 species, all with prickly stems, leaves, yellow flowers and capsules. *Argemone mexicana* L., commonly known as Mexican or prickly poppy, is native to tropical America, but has widely spread in India and Southeast Asia. It is frequently found as a weed in cultivated and abandoned fields. It is an annual, hermaphroditic shrub, mostly pollinated by

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insects, with terminal bright yellow flowers (Rao and Dave, 2001). It is found everywhere as weed in forest land, unutilized public land such as along railway roads, irrigation canals, field boundaries and fallow land of the farmers. Seeds are rich in non-saturated fatty acids, such as linoleic, oleic, ricinoleic, and palmitoleic acids. Nevertheless, their high content of toxic compounds may hamper their use with industrial purposes. In fact, the presence of *A. mexicana* oil in edible mustard oil is probably responsible for outbreaks of epidemic dropsy; a clinical syndrome characterized by edema, cardiac insufficiency, renal failure and glaucoma, which is attributed to sanguinarine, the main *Argemone* alkaloid (Garcia et al., 2006). Sanguinarine is a quaternary benzophenanthridine alkaloid with a strong bactericidal effect on Gram-positive bacteria (Rao and Dave, 2001). It also displays anti-inflammatory and cytotoxic activities. The antimicrobial and physiological effects of sanguinarine suggest that it may confer protection against diverse pathogens (Facchini, 2001). Other identified alkaloids in *A. mexicana* include berberine, protopine and coptisine (Facchini, 2001). The complex alkaloid mixture of this plant is perhaps the basis for its allelopathic, nematocidal and bactericidal effects. In this way, *A. mexicana* has many potential uses, some of them derived of the presence of alkaloids, while others may be handicapped by these same toxic compounds. A considerable amount of work has been done on studying ester and biogas generation from plant biomass. No detailed study, however, have been made so far on use of seeds and its waste of same plant for generation of both ester and biogas.

MATERIALS AND METHODS

Material

The seeds of *A. mexicana* were taken as sample for this investigation plants samples were grown in Botanical garden of Devi Ahilya University, Indore during December to March, 2007. Seeds of *A. Mexicana* were collected from wastelands near Indore City.

Methods

Crop pattern and yield assessments

The seedlings of *A. mexicana* were raised and transplanted in the botanical garden field in one meter by one meter beds, of Black Cotton soil, with interspacing of 50 cm from line to line and plant to plant with approximate 25 g of different manures like urea, N.P.K., P2O5.

Extraction and purification of oil

The oil was obtained from the seeds by the solvent extraction process using petroleum ether as a solvent (40-60 °C) by Soxhlet apparatus (Southcombe, 1962). For purification, the oil taken in a separating funnel along with water (100 ml), ether (200 ml) and

saturated sodium chloride, the content was shaken well and allowed to stand. The aqueous layer was discarded and the process was repeated twice with organic layer. Finally, the ethanol extract was taken in a conical flask and dried over anhydrous sodium sulphate (20 g) and was evaporated at 40 °C to get purified oil. For making it more economic, the oil can be extracted by expeller.

Laboratory preparation of ester from A. mexicana oil

Ester is extracted by the process (Ma and Hanna, 1998) of transesterification of oil. In transesterification of oil, triglycerides react with an alcohol in the presence of a strong acid or base, producing mixture of fatty acid alkyls ester and glycerol.

Proximate analysis of A. mexicana seed

The total solid moisture content and volatile matter of *A. mexicana*, seed waste is determined by standard methods (Chichilo and Reynolds, 1970). Two grams of the sample were taken in a silica crucible and dried in an air oven to constant weight at 105 - 110 °C for five hours. The weight of the residue was reported as the total solid content of the material.

The difference in weight between the sample and the residue is the moisture content. Volatile matter and ash content of the waste were determined using a muffle furnace maintained at 550 °C. Covered and opened Petri dishes were used to hold the sample in the furnace for the determination of volatile matter and ash content respectively. Volatile matter and ash content were determined by taking the difference between weight of samples taken and the residue left in respective experiments.

Determination of Calorific value of A. maxicana seed waste and oil

A bomb calorimeter (Tosniwal make) was used to measure the gross heating value of seed waste and liquid fuels. A weight amount sample contained in a gelatin capsule was burnt in oxygen in bomb calorimeter. The calorimeter was calibrated by the combustion of known calorific value fuel (benzoic acid). High heating value of gelatin capsule was measured before starting the tests with the oils/Biodiesel sample. The weight of different oils/Biodiesel samples contained in the capsules varied from 0.5 to 0.60 g. Detail of the procedure employed for the calculation /measurements including the correction factors were already known Final report of ICAR Adhoc scheme (1998) and Gupta (1994).

Determination of flash point and fire point of A. mexicane oil

Flash point is the temperature at which a material gives sufficient vapors which, when mixed with air, form an ignitable mixture and give a momentary flame on the application of a small pilot flame. Flash point of the liquid fuels was measured by "pensky marten" flash point (closed type) apparatus of toshaniwal make. The liquid fuels were filled in a test cup up to the specified level. It was heated at a slow and constant rate with continuous stirring up to a temperature when fumes started coming. A small test flame was directed on to the cup at regular intervals. Flash point was taken as the lowest temperature at which the application of the test flame caused the vapor above the sample to ignite momentary.

Determination of viscosity of A. mexicana ester and oil

Redwood viscometer No.1 was used for measurement of

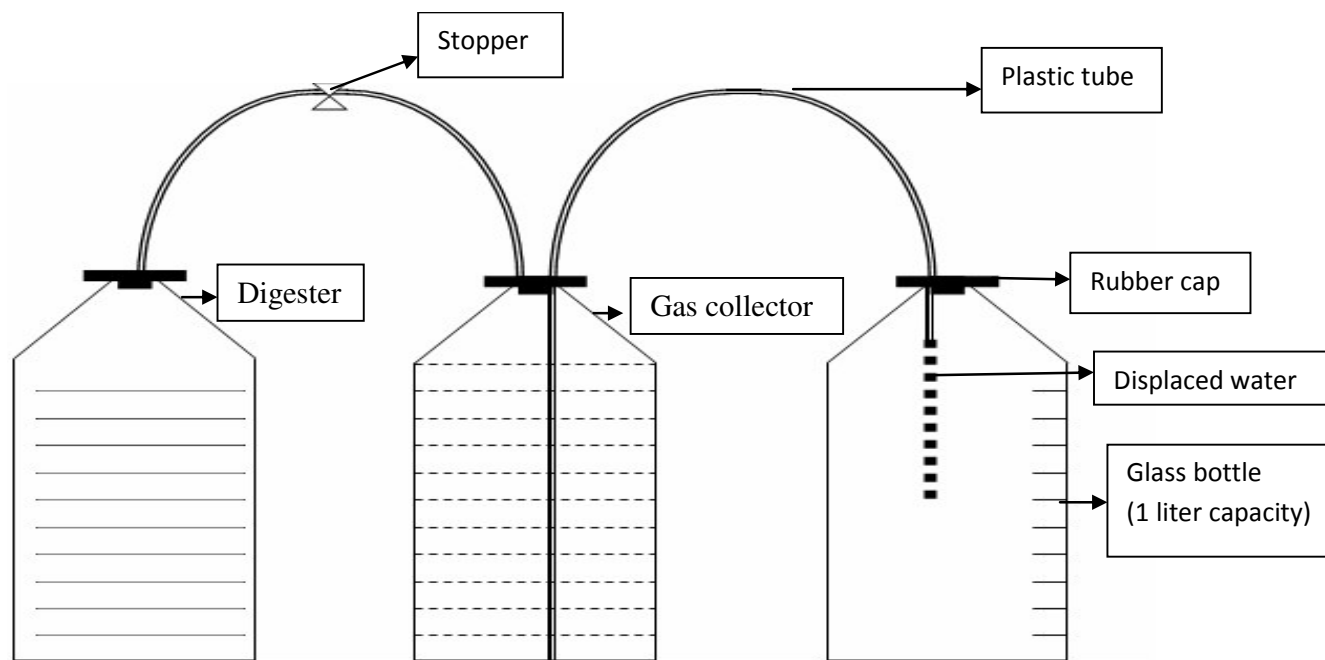


Figure 1. Reactor design (see experimental set up).

kinematics viscosity of liquid fuels. This apparatus was based on the principle of measuring the time of gravity flow (in second) of a fixed volume (50 ml) of fluid through a specified hole made in a jet piece (as per IP 70/62 issued by institute of petroleum London). The apparatus could be used for flow times between 30 and 2000 s. A metallic ball was provided to open and close the jet. Two thermometers, one each for the paraffin jacket and the oil cup, were also provided. A standard 50 ml volumetric glass flask was kept below the jet to collect the flowing oil. Each test was replicated three times. The mixtures of liquid fuel were heated to different temperatures starting from ambient to a maximum of 100°C. Kinematics viscosity in Centistokes (cS) was calculated from the time units by the following formula:

$$V_k = 0.26-179/t, \text{ when } 34 < t < 100$$

And

$$V_k = 0.24-50/t, \text{ when } t > 100$$

Where, V = Kinematics viscosity in Centistokes (cS), T = Time for flow of 50 ml samples in seconds.

High viscosity is one of the major constraints for the long duration use of plant oils and their esters as a fuel in diesel engines. Since viscosity is temperature dependent, the effect of temperature on viscosity of plant oils, esters and their mixture with diesel was studied.

Determination of density of *A. mexicana* ester and oil

Density of oils and their ester was measured by means of relative density bottles of 50 ml capacity (of borosil make). The relative density bottle was first completely dried and weighed. It was then filled with the liquid fuels at different temperatures and capillary stopper was placed gently on the neck of the bottle with taking precaution that no air bubble was left inside the bottle. The bottle

was then cleaned from outside with the help of filter paper and weighed. Density was calculated from following equation:

$$d = (M_2 - M_1) / 50$$

Where d = density of samples in g/ml, M_2 = mass of relative density bottle + liquid fuels in gram (g), M_1 = mass of empty relative density bottle in gram (g).

Gas analysis

The product biogas composition was analyzed by gas chromatograph (Amil modal no 5700) using thermal conductivity detector with a Poropak-Q column. Hydrogen was used as carrier gas at a flow rate of 20 ml per minute. The oven, injector and detector temperature were maintained at 80, 120 and 140°C respectively.

Experimental set up

Reactor design for biogas

The experimental setup for biogas production comprised of one liter graduated glass bottles fitted with rubber caps (Figure 1). The bottle was connected with plastic tube to take away gas from the digester to the gas collector and displace water from the gas collector to another bottle. A flow regulator or stopper in the form of a plastic tube was used as a clip while refilling the bottle.

The stoppers were placed open in soft tubes connecting the digesters to the gas collector bottle (Singh et al., 2006). 250 g seed waste mixture with water was taken in both bottles. Biogas produced in the digesters was measured once daily by reading the label of displaced water in the glass bottle. The digester bottles were placed in sunlight as well as at room temperature (16-20°C) for 33 days. The methane content in the reactor was 52%. The biogas yield in both the reactors was 3 L, 650 and 260 ml

Table 1. Amount of ester and glycerol extracted from *A. mexicana* oil.

Non edible oil (1 L)	Alcohol (200 ml)	Catalyst	Ester (ml)	Glycerol (ml)
<i>A. mexicana</i>	Methanol	NaOH	1000	200
<i>A. Mexicana</i>	Ethanol	KOH	700	500

Table 2. Parameters for *A. mexicana* oil and its esters.

Parameters	<i>A. mexicana</i> oil	<i>A. mexicana</i> methyl ester	Diesel
Calorific value (kcal/kg)	8,463	9,753	10,693
Flash point (°C)	235	170	66
Fire point(°C)	260	210	89
Density (Gm/ml)	0.91	0.87	0.78
Viscosity (Centistock)	29.6	10.2	4.33

respectively. A temperature sensing display unit was also hanged for temperature readings.

RESULTS AND DISCUSSION

A. mexicana is one of the promising drought tolerant annual wild herb and adaptable to various kind of soil condition. It grows well on roadside, wasteland so that their production does not exert any pressure on agriculture lands. It does not require much care and its cultivation is not much expensive. The plant is grown directly from seeds. The proper time for seed germination is month of December. A total of 30% of oil was extracted from fresh seeds of *A. mexicana*, through the Soxhlet apparatus as mentioned in material and method. This oil was then converted into methyl ester by the process of transesterification. *A. mexicana* methyl ester showed the better fuel properties compared to the oil. The maximum yield of ester was obtained using NaOH a catalyst at a concentration of 0.35 g per 100 ml of crude oil diluted 5:1 with methanol, at 60°C. Methanol is better separation media as compared to ethanol (Table 1).

Methanol, used to produce methyl ester, not only produced better results than ethanol, but also is cheaper than ethanol, which is an important consideration for commercial purposes. Both moieties, the fatty acid and the alcohol, functionally contribute the overall properties of a fatty ester (Knothe, 2005).

The calorific values of methyl esters are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. Calorific value of *A. mexicana* oil is low (8,463 Kcal /Kg) as compared to its ester (9,753 Kcal /kg) and petroleum diesel (10,693 Kcal/Kg).

Biodiesel has a higher flash point compared to diesel. It is the temperature at which a fuel will catch fire; because biodiesel has a high number of fatty acid methyl esters, which are generally not volatile. The flash point in the oil

was very high (235°C) as compared to its ester (170°C) and diesel (66°C). The degree of unsaturation in the esters showed little effect on the flash point. The higher flash point of the ester fuels suggests that the fuels were less flammable than diesel and therefore safer to store and handle. The flash point of fuel is not directly related to engine performance. This parameter reflects a fuel's safety, the higher the flashpoint the less likelihood the fuel will accidentally ignite. Diesel fuel has showed a lowest flashpoint, while biodiesel and its blends generally possess greater flashpoint values (Graboski and McCormick, 1998).

The molecular weight of a typical ester molecule is roughly one-third that of a straight vegetable oil molecule and has viscosity approximately twice that of diesel fuel instead of 10–20 times as in the case of neat vegetable oils (Peterson, 1986). Viscosity in the oil was higher (29.6 Cst), compared to ester (10.2 Cst) and diesel (4.33). The values of viscosity show that the seed oils are more viscous than diesel and have a lower ignition quality. When the oil is transesterified with methyl alcohol and catalyst of biodiesel, which is similar to diesel. Transesterification reduce the viscosity. The viscosity of biodiesel is slightly greater than that of petro-diesel but approximately an order of magnitude less than that of the parent vegetable oil or fat (Knothe and Dunn, 2001). The fuel viscosity controls the characteristics (droplet size, spray) of injection from the injector. Oil also shows higher (0.91 g/ml) density compared to ester (0.87 g/ml) and diesel (0.73). The density of biodiesel as compared to the petro-diesel is higher which indicate combustion efficiency of bio-diesel. Increased combustion efficiency result in lower emission of unburnt hydrocarbons. All the parameters of *A. mexicana* are summarized in Table 2.

A. mexicana seed waste was used as sample for biogas production. Calorific value of seed waste was 4,621 Kcal/Kg. All the parameters of seed waste were studied, which are summarized in Table 3. The methane content in the reactor was 52%. The biogas yield in both

Table 3. Parameters of *A. mexicana* seed waste.

Calorific value kcal/kg	Moisture (%)	Volatile matter (%)	Ash (%)	C: N ratio
4621	3.185	90.742	9.334	11.0

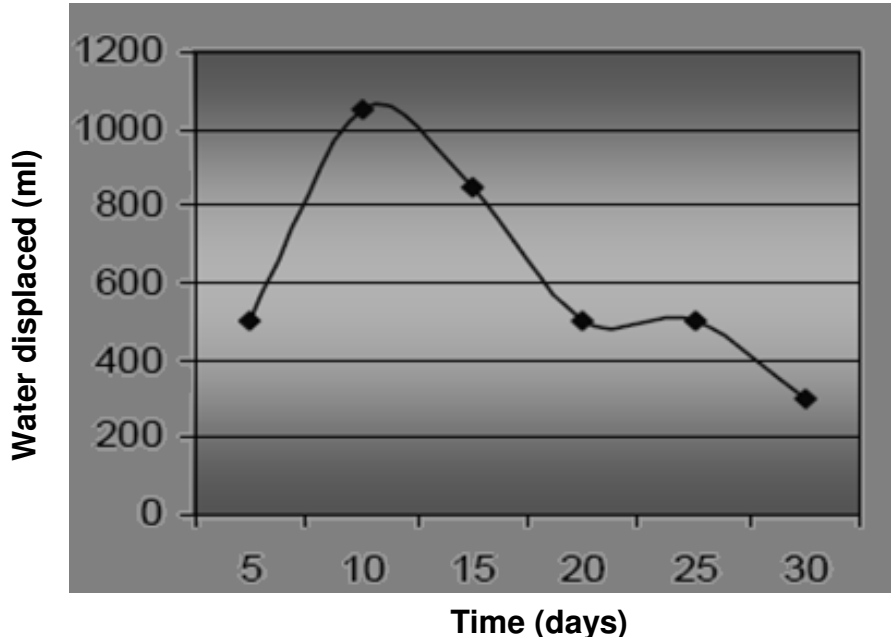


Figure 2. Cumulative biogas production in sunlight (21-30°C).

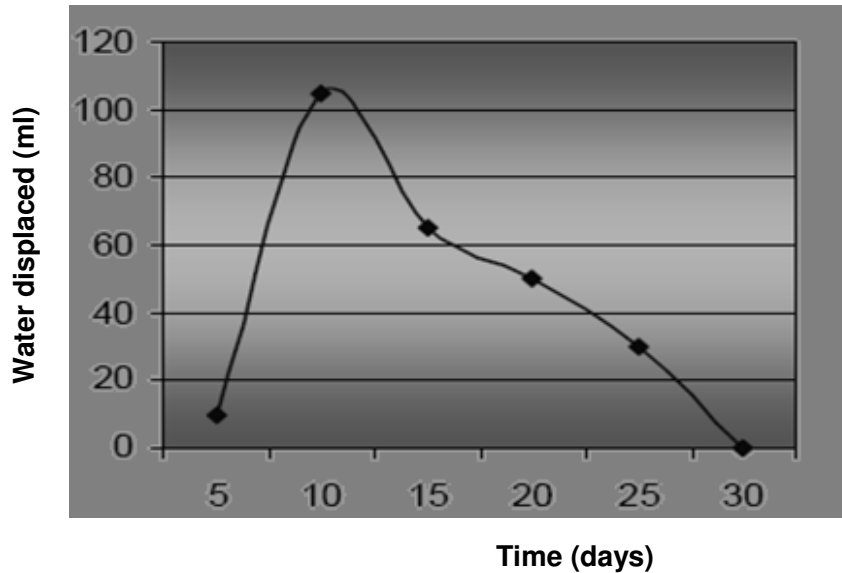


Figure 3. Cumulative biogas production at room temperature (16-20°C).

the reactors was 3 L, 650 and 260 ml respectively. Figures 2 and 3 shows the graphical representation of the water displacement of each day. Biogas production

changed according to temperature. The reactor placed in sunlight showed better result because sunlight increases the biogas production. Biogas yield increased day by day

and it reached its highest volume after 10 days and after 10 days production decrease slowly because all matter which responsible to produce methane gas decreased and its effect the production rate.

Conclusion

This is the first study reporting utilization of *A. mexicana* seed waste for both biogas and ester. Our study showed that *A. mexicana* seed contains 30% oil which can be used for the production of methyl ester. The seed waste can then be utilized to produce biogas containing 52% methane. From the result, we can conclude that the *A. mexicana* is a viable source for production both ester and biogas. Biogas producing efficiency of *A. mexicana* seed waste is higher in sunlight (22- 30°C) than at room temperature (16-20°C). This could be further studied at pilot plant scale in controlled temperature for commercial use.

REFERENCES

- Chichilo P, Reynolds H (1970). Associate editors Fertilizers in Official methods of Analysis of the association of official analytical chemists 11 ed Horwitz W (editor) Washington Association of official analytical chemist, pp. 16-20.
- Facchini PJ (2001). Alkaloid biosynthesis in plants: biochemistry, cell biology, molecular regulation, and metabolic engineering applications. Annual Rev. Plant Physiol. Plant Mol. Biol., June, 52: 29-66.
- Final report of ICAR Adhoc scheme (1998). In "studies on bulk production and use of selected plant oil esters as alternate renewable fuel for diesel engines". submitted by Dept. FPM, COAE, PAU, Ludhiana.
- Garcia VP, Valdes F, Martin R, Luis JC, Afonso AM, Ayala JH (2006). Biosynthesis of antitumoral and bactericidal sanguinarine. J. Biomed. Biotechnol., 635(18): 1-6.
- Graboski MS, McCormick RL (1998). Combustion of fat and vegetable oil derived fuels in diesel engines, Prog. Energy Combust. Sci., 24: 125- 164.
- Peterson GL (1986). Vegetable oil and diesel fuel: status and research priorities. h n s ASAE, 29(5): 1413-22.
- Gujer W, Zehnder AJB (1983) Conversion process in anaerobic digestion. Water Sci. Technol., 15: 127-67.
- Gupta PK (1994). "Investigation on methyl esters of plant oils as alternative renewable fuel for compression ignition engines" Unpublished Ph.D. thesis, Dept. of FPM, PAU, Ludhiana (India).
- Klass DL (1998). Biomass for renewable energy, fuels, and chemicals. New York: Academic Press, p. 333.
- Knothe G, Dunn RO (2001). In: F.D. Gunstone, R.J. Hamilton (Eds.), Oleochemical Manufacture and Applications, Sheffield Academic Press, Sheffield, UK, p. 106.
- Knothe G (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process Technol., 86: 1059-70.
- Ma F, Hanna MA (1998). Biodiesel production, a Rev., Bioresour. Technol., 70: 1-15.
- Meher LC, Vidyasagar D, Naik SN (2006). Technical Aspect of Biodiesel production by transesterification-A Rev. Renewable Sustainable Energy Rev., 10: 248-268.
- Rao TVR, Dave YS (2001). Morpho-histogenic studies of the fruit wall of *Argemone mexicana* L. (Papaveraceae). Acta Botanica Hungarica, Sept., 43(3-4): 391-401.
- Southcombe JE (1962). Chemistry of oil industries, constable and Co. Ltd. London, p. 144.
- Singh SP, Tyagi S, Rathod NS (2006). A Study on the combined effect of Mg and Zn metal catalyst on Biogas production. SESI, 6(2): 35-42.
- Srivastava A, Prasad R (2000). Triglycerides- based Diesel fuels. Renewable Sustainable Energy Rev., 4: 111-33.
- Yadvika S, Sreekrishnan TR, Sangeeta K, Vineet R (2004) Enhancement of biogas production from solid substrates using different technique-A Rev. Bioresour. Technol., 95: 1-10.