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A RENEWABLE DIESEL FROM ALGAE: SYNTHESIS AND CHARACTERIZATION OF BIODIESEL IN SITU TRANSESTERIFICATION OF *CHLORO PHYCOPHYTA (GREEN ALGEA)* USING DODECANE AS A SOLVENT

V.Naresh[1], S.Phabhakar[2], K.Annamalai[3], S.Naveen Chandra[4]

[1,2,3,4]*Assistant Professor, Bharathidasan Engineering College, Nattrampalli*

ABSTRACT

In situ transesterification of Chloro phycophyta (green algea) *was performed using 5–20 wt% sulfuric acid as a catalyst at either 60 or 100 °C. The maximum ester yield in the range of 96–98% is comparative to the specification of ester content in biodiesel, 96%. A high excess of methanol was used in transesterification ensured also a high ester yield. The FAME was purified via adsorption of* Chloro phycophyta *and carotenoids onto a clay. Properties of the purified biodiesel were investigated with several methods. The results showed that the* Chloro phycophyta (green algea) *based biodiesel exhibits slightly lower oxidative and thermal stability compared to soybean based biodiesel due to the presence of polyunsaturated FAME. In addition to biodiesel, also the residual biomass was characterized showing that it contained sugars and proteins. An additional hydrogenation would increase the oxidative stability. Hydrodeoxygenation of* Chloro phycophyta (green algea)*based biodiesel was also demonstrated over 5 wt% Ni–HY-80 zeolite with SiO_2/Al_2O_3 ratio of 80 and with 5 wt% Pd/C at 300 °C and 30 bar in dodecane as a solvent. Ni–HY-80 was superior to Pd/C catalyst giving more than 95% yield of hydrocarbons.*

Keywords: Algae; Biodiesel; Trans esterification

I. INTRODUCTION

Biodiesel is a clean-burning, renewable fuel made from vegetable oils,animal fats and recycled cooking oil and greases. The manufacturing process for biodiesel combines oils and fats with methanol and a catalyst to produce fatty acid methyl esters, which is commonly referred to as biodiesel. Vegetable oils such as rapeseed, canola, soybean and palm oil are the most common raw material for commercial-scale biodiesel production Much earlier, in 1853 scientists E. Duffy and J. Patrick, conducted the transesterification of a vegetable. This was many years before the first diesel engine even became serviceable. According to the **history of biodiesel** fuel, Rudolf Diesel's prime model ran on its own power for the first time in Germany in 1893. Biodiesel is typically used as an additive to conventional diesel fuel, ranging in content from 2% to 50% or more. Consequently, biodiesel fuel is often referred to by the percentage of biodiesel in the fuel.

For example, B20 is a blended fuel that contains 20% biodiesel and 80% conventional diesel. B20 is a common blend because it provides a good balance between costs, performance, and environmental benefit .

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II. REDUCES HARMFUL EMISSIONS AND POLLUTANTS

Biodiesel fuels reduce emissions of various pollutants and global warming gases such as CO, CO2, hydrocarbons and particulate matter by as much as 50% compared to conventional diesel 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.

OIL + (METHANOL + **DODECANE)** → **BIODIESEL** + GLYCERIN

SI NO.	PROPERTIES	**DODECANE**
1	APPEARANCE	liquid
2	MOLECULAR MASS	170.33484 g/mol
3	COLOUR	Clear White
4	BOILING POINT	216.3^{o} F
5	FLASH POINT	165^{O} F
6	CRITICAL TEMPERATURE	421.3°F
7	SELF IGNITION TEMPERATURE	397 ^{O} F
8	DENSITY	0.7495 g/cu cm
9	VISCOSITY	1.34 mPa s
10	FORMULA	$C_{12}H_{26}$

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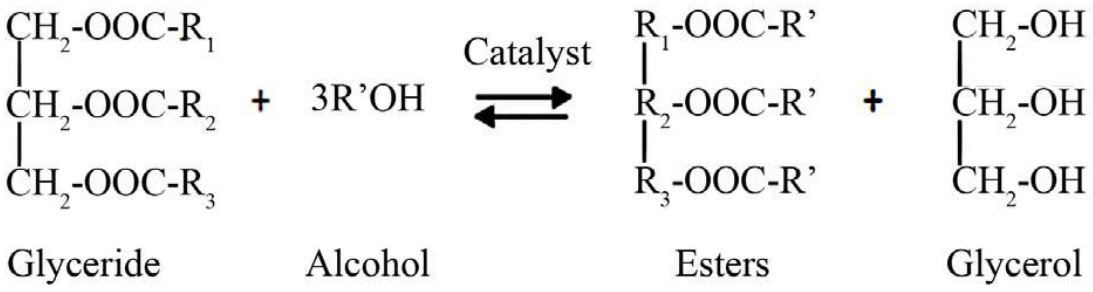
Comparison of Fuel Properties

Properties	Gasoline	Methanol	Ethanol
Chemical Formula	C_8H_{15}	CH_3OH	C_2H_5OH
Molecular Weight	111.21	32.04	46.07
Oxygen Content, wt. %	-	49.93	34.73
Carbon Content, wt. %	86.3	37.5	52.2
Hydrogen Content, wt. %	24.8	12.5	13.1
Stoichiometric AFR	14.5	6.43	8.94
Lower Heating Value, MJ/kg	44.3	20	27
Heat of evaporation, kJ/kg	305	1178	840
Research octane number	96.5	112	111
Motor octane number	87.2	91	92
Vapor pressure (kPa)	61.4	32.4	19.3

III. TRANSESTERIFICATION PROCEDURE

Vehicular pollutant emissions caused by the combustion of fossil fuels and crude oil price fluctuations brought into focus the need for developing alternate fuels which could create less pollution, produced from renewable feedstocks and operate without much modification in the existing design of the engine. Biodiesel (fatty acid alkyl ester) derived from transesterification of vegetable oils or an animal fat with methanol (**Figure 1**) is a potential substitute for petroleum based diesel fuels. Even 5% replacement of petroleum fuel by biofuel can save a country like India Rs. 4000 crores per year in foreign exchange Government of India has already given due importance to biofuel and announced a National Biofuel policy in year 2006. The focus is on collection and distribution of renewable feedstocks for biofuel products and R & D at pilot plant scale and later scaling upto commercial level

OIL + METHANOL → **BIODIESEL** + GLYCERIN



IV. TRANSESTERIFICATION PROCESS

Methanol and Algae oil were used as a raw material to study the effect of low frequency ultrasound on biodiesel production at 303 K, 323 K using molar ratio of oil to methanol ranging from 1:3, 1:6, 1:9 , and the quantity of **dodecane** catalyst from 1%, 2%, 3%, and 5% (wt/wt) of the weight of Algae oil. The reaction mixture consists

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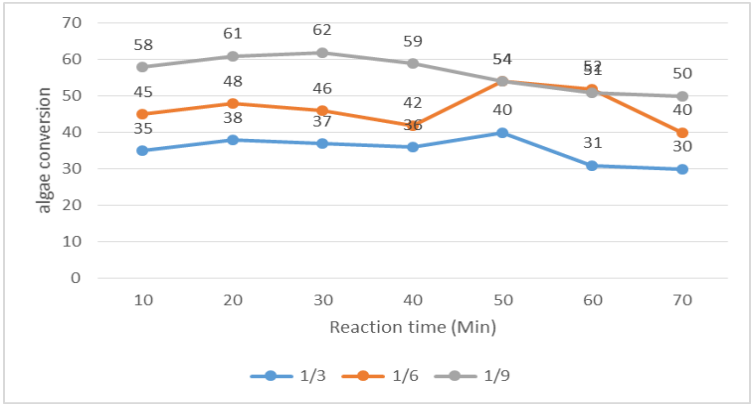
of Algae oil, methanol, and sodium hydroxide. Sodium hydroxide was dissolved into methanol followed by addition of Algae oil to the solution. Since, the Algae oil and methanol were not completely miscible, two layers were observed: the upper layer was of methanol and the lower layer was of oil.

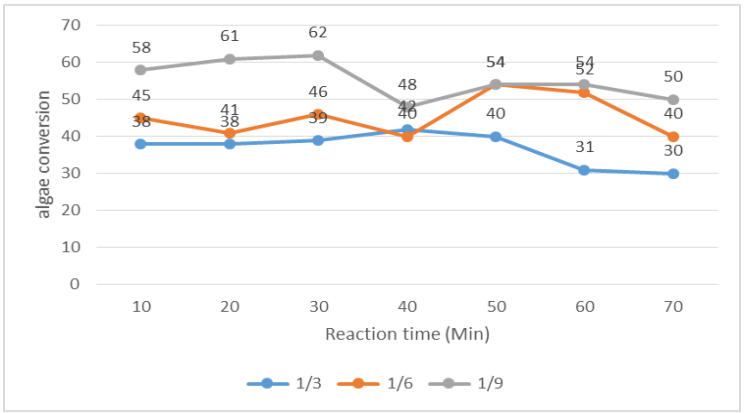
V. METHANOL TO OIL MOLAR RATIO

Stoichiometrically, the methanolysis of Algae oil requires three moles of methanol for each mole of oil.

Since, transesterification of triglycerides is reversible reaction; excess methanol is required to shift the equilibrium towards the direction of ester formation. As can be seen from (at 303 K) and (at 323 K), the maximum conversion was achieved at methanol to oil molar ratio 9:1. It is comparable to the work carried out by **L. Verma***et al.* [5] obtained 90% conversion using methanol as an alcohol with triolein oil to alcohol molar ratio of 1:6 and KOH as a catalyst. **L. Verma***et. al.* [6] have obtained above 98% yield using 1:9 Algae oil to methanol molar ratio and heterogeneous solid catalyst used was Na/SiO_2. Present study shows that with molar ratio of oil to methanol of 1:12, maximum conversion was achieved in 30 minutes only and after that it almost a constant over an extended reaction time. Molar ration of 1:3 and 1:6 are not showing good results. One of the reasons for the same may be the predominance of esterification reaction at the initial phase, to transesterify the FFA present in the Algae oil, of transesterification which can consume methanol present in the reaction mixture and hence, the amount of methanol available for transesterification may not be sufficient to drive the reaction forward for longer time.



Effect of molar ratio on conversion of algae at 303 K. Reaction conditions: Algae oil 50 g, catalyst amount 1%.



Effect of molar ratio on conversion of algae at 323 K. Reaction conditions: Algae oil 50 g, catalyst amount 1%.

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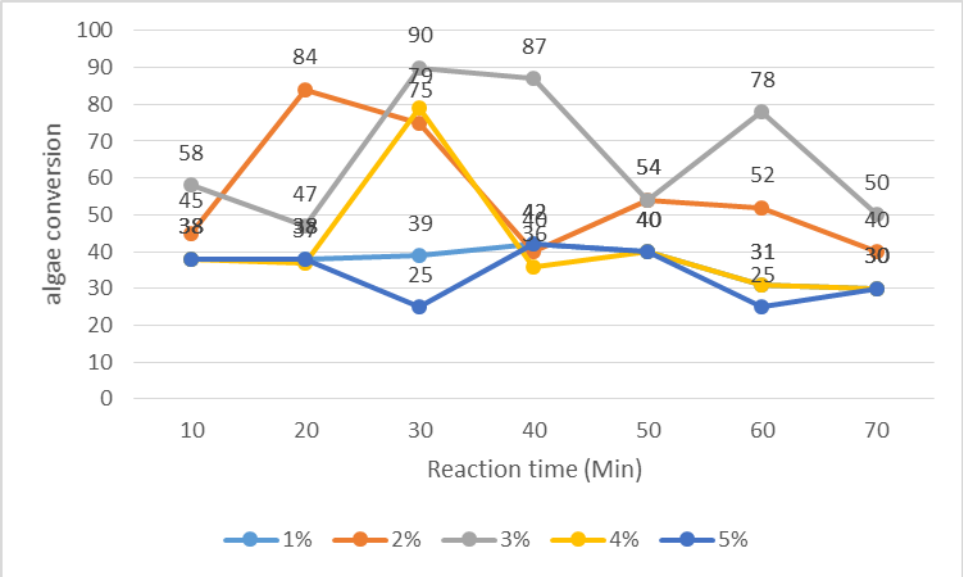
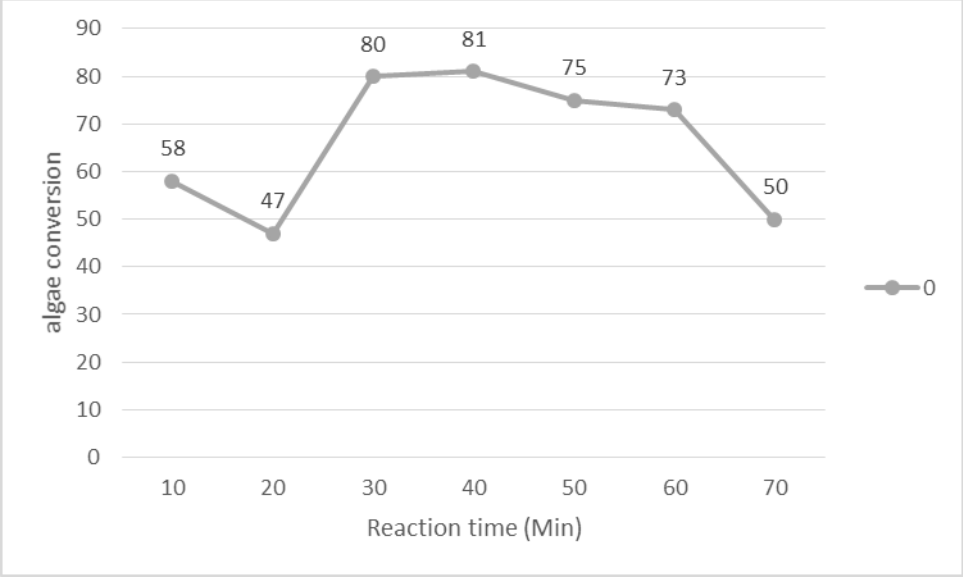
VI. AMOUNT OF CATALYST

Effect of variation of amount of catalyst on conversion was also studied. Catalyst amount was varied in the range of 0.5% to 2.5% (wt/wt of the oil taken). As shown in, the conversion increased firstly with the increase of catalyst amount from 0.5% to 1.5%. But, with further increase in the catalyst amount from 1.5% to 2.5%, the conversion decreased due to soap formation. **L. Verma***et al.* obtained their best result at 3% wt% catalyst amount which is higher than the present study. Separation of heterogeneous catalyst is adding one more stage in the process presented by **L. Verma***et al.* obtained about 90% conversion with 3% wt% of **dodecane** catalyst. The conversion obtained by them is less than what obtained in present study using same amount of catalyst at constant temperature of 323 ^{0}C



3% percentage of solvent with methanol max 90%



Zero percentage of solvent with methanol max 81%

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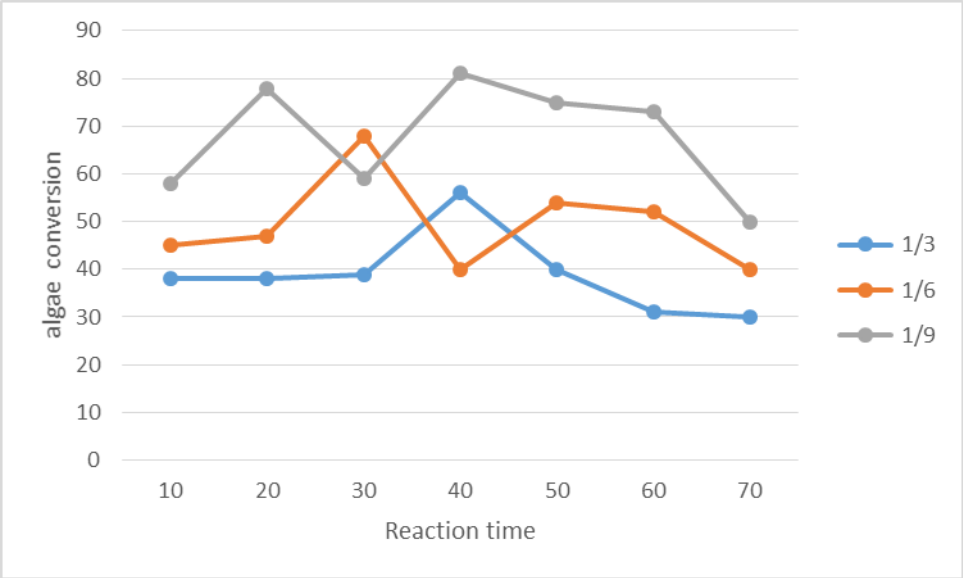
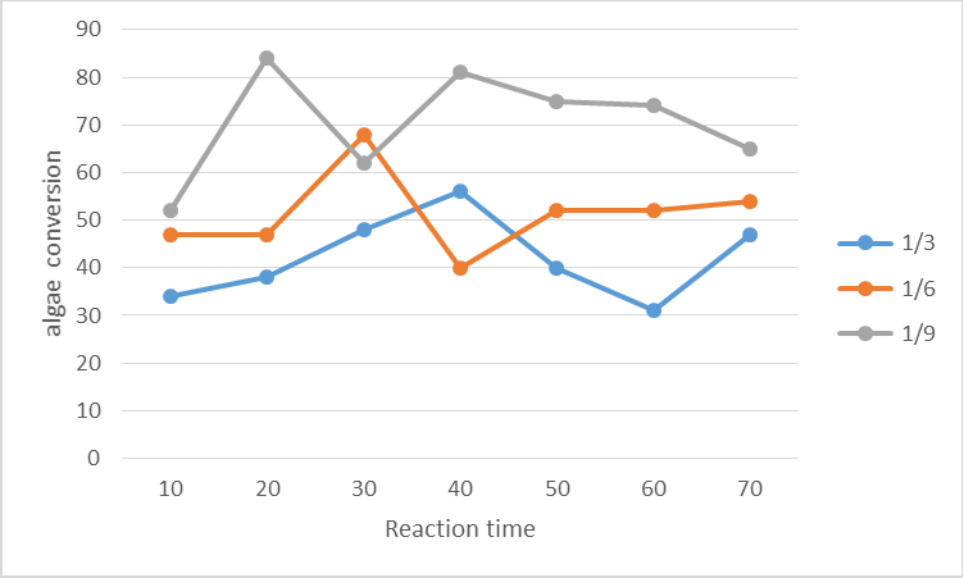
VII. ETHANOL TO OIL MOLAR RATIO

Ethanol and Algae oil were used as a raw material to study the effect of low frequency ultrasound on biodiesel production at 303 K,, 323 K using molar ratio of oil to methanol ranging from 1:3, 1:6, 1:9 and the quantity of **dodecane** catalyst from 1%, 2%, 3%, and 5% (wt/wt) of the weight of Algae oil. The reaction mixture consists of Algae oil, methanol, and sodium hydroxide. Sodium hydroxide was dissolved into methanol followed by addition of Algae oil to the solution. Since, the Algae oil and methanol were not completely miscible, two layers were observed: the upper layer was of methanol and the lower layer was of oil.



Effect of molar ratio on conversion of algae at 303 K. Reaction conditions: Algae oil 50 g, catalyst amount 1%.



Effect of molar ratio on conversion of algae at 323 K. Reaction conditions: Algae oil 50 g, catalyst amount 1%.

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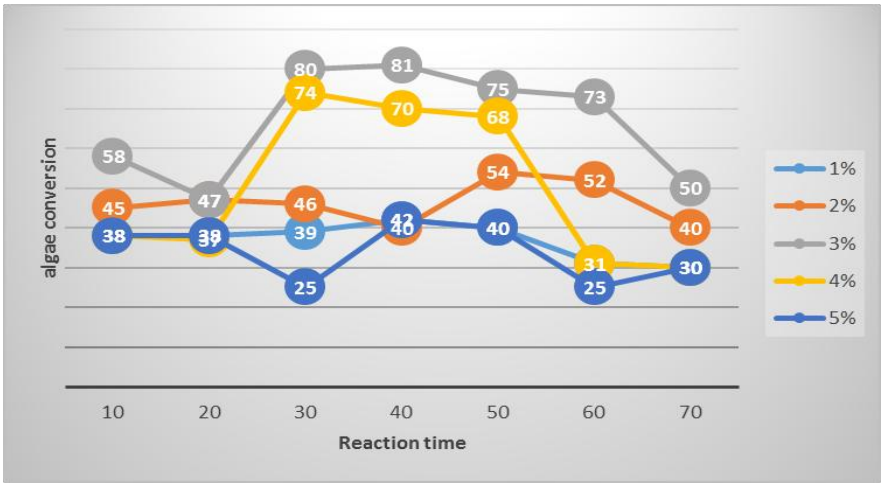
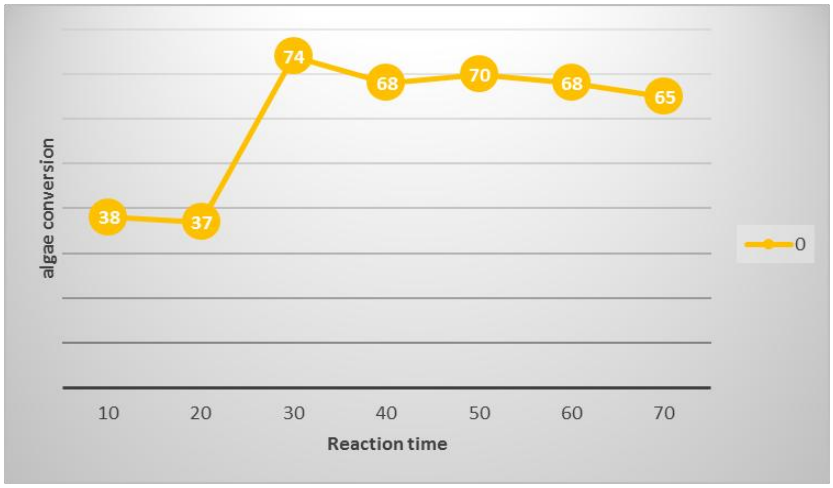


3% percentage of solvent with Ethanol max 81%



Zero percentage of solvent with Ethanol max 74%

VIII. RESULTS AND DISCUSSION

Oil	Catalyst	Alcohol	Oil to Alcohol Molar Ratio	Reaction Conditions
algae	**1%Dodecane + KOH**	Methanol	**62%**	**303K**
	KOH		**63%**	**323K**
algae	**3%Dodecane + KOH**	Methanol	**90%**	**323K**
	KOH		**81%**	**323K**
algae	**1%Dodecane + KOH**	Ethanol	**81%**	**303K**

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	KOH		**85%**	**323K**
algae	**3%Dodecane + KOH**	Ethanol	**81%**	**323K**
	KOH		**74%**	**323K**

IX. CONCLUSIONS

By the above results, we concluded that the oil extraction from different catalyst with alcohol at different molar ratio and conditions, amoung this results the methanol with 3% dodecane + koh at 323 k the oil yield is about 90%. From normal reactio 9% more oil conversion can be abtain using this dodecane catalyst.

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