PRODUCTION OF MONOGLYCERIDES FROM GLYCEROL OBTAINED FROM BIODIESEL PROCESSING

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by

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Dedicated to

My Munuma

for her endless support and encouragement

The Almighty who blessed me with the ability and strength to accomplished it

CERTIFICATE

This is to certify that the thesis entitled, **"PRODUCTION OF MONOGLYCERIDES FROM GLYCEROL OBTAINED FORM BIODIESEL PROCESSING"** being submitted by **Mr. Malaya Kumar Naik** to the Indian Institute of Technology Delhi for the award of Doctor of philosophy is a record of bonafide research work carried out by him under our guidance and supervision n conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or in full, to any other university of institute for the award of any degree of diploma.

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(Malaya Kumar Naik)

ABSTRACT

Chemistry has the key role of playing, maintaining and improving our quality of life with minimizing the effect on environment. In the recent year, the establishment of new technology on green chemistry has better impact on environment for sustainable development. This will realize the discovery and development of new synthetic routes through renewable sources.

Emulsifiers, important class of chemical are having multiple applications in household, industrial and agricultural sectors and can be derived from both petrochemical and oleochemical resources. Renewable resources have better advantage as contribute less to the greenhouse gases.

They have wide applications because of their surface-active properties. They are composed of a water-soluble polar group, the hydrophilic portion, and a hydrocarbon chain, the hydrophobic portion, which provide the compound an interfacial activity to bind both polar and non-polar compounds together. It has wide utilization in pharmaceutical, cosmoceutical, agricultural and industrial applications. For instance, has application in detergents, cosmetics, also used as antistatic agents, lubricants, paint, textile production, as a flotation agents in mining, oil production and wastewater treatment and as emulsifiers in the food industry and for the production of colorants, coatings and plastics. It is also widely used in the manufacturing of pesticides, herbicide, fungicide and rodenticides in agrochemical industries.

Commercial emulsifiers were introduced in the 1930s in the form of monoglycerides and glycerolysis of triglycerides is one of the suitable chemical routes from others for its preparation. The homogenous and heterogeneous catalysis routes were found unsuitable and uneconomical due to involvement of high temperature leading to the formation of low quality and quantity of monoglycerides. Enzymatic glycerolysis, a suitable technology awarded comparatively high quality and quantity of the desired product.

Glycerol, a main by-product from the biodiesel industries and about 3.7 billion gallons are available globally. Thus, to utilize the surplus amount of by-product glycerol, glycerolysis with vegetable oil is one best route to produce the monoglycerides fractions. Due to the governmental initiatives and other programmes, Jatropha oil seed production have increased to large excess and thus, could be suitable to utilized as a feedstock for the above reactions. Besides Jatropha, other oils could also be used for monoglycerides preparation for the desired applications, likewise, for food or pharma based applications, edible grade oil would be beneficial and for non-pharma or non-food based applications non-edible vegetable oils will be

suitable. In India, as Government imports more than 80% of its edible grade oils for its domestic applications, thus, in case application of edible grade oil in non-food based applications would not be an economical way. To overcome this problem, steps were taken to produce the monoglycerides fractions utilizing by-product glycerol and non-edible grade vegetable oils.

It is known that, vegetable oils with interval of times, very prompt to oxidize and hence the quality deteriorate. Thus, to compare the monoglycerides formations through different qualities of oils, two types of glycerolysis were carried out, i.e. (a) glycerolysis of low free fatty acid Jatropha oil with analytical grade glycerol and (b) glycerolysis of high free fatty acid Jatropha oil with by-product glycerol (85% pure). During the reaction, the indigenous Fermase CALB 10000 enzymes were used to minimize the production cost.

In the reaction, low free fatty acid Jatropha oil with analytical grade glycerol, the parameters varied were catalyst concentrations (5-20 wt %), oil to glycerol molar ratio (1:1 to 1:15), cosolvents types, oil to cosolvent molar ratio (1:10 to 1:40), reaction temperature (20-80 ^{0}C), reaction time etc, keeping mixing speed fixed at 200 rpm. In the optimum condition, the monoglycerides yield was found 72-76% with 13-17 % of diglycerides and remaining with free fatty acid, unreacted glycerol and triglycerides.

In the reaction, high free fatty acid Jatropha oil with by-product glycerol (85% pure), the optimization were carried out by response surface methodology. The optimum parameters were 20 wt % catalyst concentrations, 1:30 oil to cosolvent ratio and 1:7 oil to glycerol ratio giving the monoglycerides yield 55-60%, diglycerides 30-35% and triglycerides 7-10% with some free fatty acids and glycerol. The same reactions, continued with dehydrating agents improved the monoglycerides formation by 65% with anhydrous sodium sulphate and 70% with silica gel. This was because of the quality of silica gel having better dehydrating property than anhydrous sodium sulphate.

For better applications, the monoglycerides fractions from its mixture were purified by column chromatography and molecular distillation apparatus. Column chromatography apparatus gave more than 96% purity of monoglycerides fractions, but the duration of purification and consumption of organic solvents makes this methodology environmentally unsuitable.

Purification of monoglycerides through molecular distillation apparatus found 83-85% monoglycerides, 6-9% diglycerides, 6-8% triglycerides (6-8%) at flow rate of 4-6 g/min and 79-81% monoglycerides, 8-12% diglycerides, 10-12% triglycerides at 7-8 g/min flow rate. The optimum parameters were 210 ^{0}C distillation temperatures; 35-40 °C feed temperature, 25-28 °C condenser temperature at 8 mTorr vacuum. Even on varying the vacuum and distillation temperature, did not improve the purification of monoglycerides fractions significantly. The above optimum parameters were found suitable with feedstock mixture having different percent of monoglycerides fractions (i.e. 33%, 45% and 58%), giving similar percents of monoglycerides fractions in the final product, which indicates the superiority of the optimized parameters.

The purified fractions enriched with monoglycerides fractions showed better physico-chemical properties like acid value, induction period, iodine value, saponification value etc. and based on the hydrophilic-lipophilic balance was found suitable in O/W emulsions.

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NOTIONS

BIS	Bureau of Indian Standard
ASTM	American society for testing and materials
@	At (the rate)
~	Approximately
SCF	Supercritical fluid
KG	Kilogram
cm	Centimeter
Conc.	Concentration
^{0}C	Degree centigrade
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FA	Fatty acid
GC	Gas chromatography
HPLC	High performance liquid chromatography
Min	Minute
Hr	Hour
K	Kelvin
MT	Metric ton
MJ/KG	Mega joule per Kilogram
MAG	Monoglycerides
DAG	Diglycerides
TAG	Triglycerides
GL	Glycerol
LA	Lauric acid
OA	Oleic acid
SA	Stearic acid
FT	Feed temperature
CT	Condenser Temperature