بسم الله الرحمن الرحيم

Sudan University of Science &Technology

College of Science

Department of Scientific Laboratories - Chemistry

PRODUCTION OF BIODIESEL FROM NEEM SEEDS OIL

إنتاج الوقود الحيوي من زيت بذور النيم

Research submitted for the requirements of the Bachelor degree in scientific laboratories – Chemistry

Prepared by:

Amira Loay Abdulla
Randa Fatthi Hamid
Rofida Magzoub Ali

Supervisor:

Dr. Fatthi Abass

October 2016

الآيـة

يقول الله سبحانه و تعالى:

(هُوَ الَّذِي أَنْزَلَ مِنَ السَّمَاءِ مَآءً لَّكُم مِّنْهُ شَرَابٌ وَمِنْهُ شَجَرٌ فِيهِ تُسِيمُونَ)

صدق اللّه العظيم

سورة النحل الايه (10)

Dedication

To my all relatives and friends

To my parents.

To my sisters and brothers.

To all who helped me throughout this dissertation.

Acknowledgements

The researchers would like to express his gratitude to the supervisor **Dr. Fatthi Abass.**

Thanks also are extended to Teacher Reem Mohammed Ahmed for her continuous Helping, and thanks are also extended to all teachers and Employees in Sudan University of Science & Technology Faculty of Forests and Victuals.

Thanks are also due to my friends and to my teacher who taught how to read.

Abstract

Neem oil was extracted by soxhelt from neem seeds and it is application such as esterification in the industry of biodiesel and it is inalyzed using spectroscopic methods like UV/VIS and IR to identify the functional group also using thin layer chromatography and determined the physical properties of biodiesel, and it shows affinity with standard sample .

ملخص الدراسة

تم إستخلاص زيت النيم من بذور النيم باستخدام جهاز السوكسوليت وتمت أسترة الناتج لإنتاج الوقود الحيوي وتم التعرف على الزمرة الموجودة في مركب الوقود الحيوي بإستخدام الطرق المطيافية التي تتمثل في الأشعة تحت الحمراء والأشعة فوق البنفسجية، وتم أيضا التعرف بواسطة الطرق الكروماتوغرافية بإستخدام تقنية الطبقة الرقيقة وتم تقدير الخواص الفيزيائية للوقود الحيوي وأظهرت التقارب مع العينة القياسية.

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CHAPTER ONE
Introduction

1. Introduction

1.1 NEEM

1.1.1 LOCAL NAMES

Amharic (kinin); Arabic (nim, neem); Bengali (nimgach, nim); Burmese (bowtamaka,thinboro, tamarkha, tamar, tamaka, tamabin); Cantonese (nimba,kohomba,bevu); Chamorro (sdau); Creole (nim); English (Persian lilac,neem tree,bastard tree, Indian lilac, bead tree, margosa tree, cornucopia, Indian cedar); French (margousier,margosier, neem,nim,azadirac de l'Inde); Hindi (neem, balnimb, nim, veppam, nind, vempu); Indonesian (mind, intaran, membha, imba, mempheuh, mimba); Javanese (mimba, imba); Khmer (sdau); Lao (Sino-Tibetan) (ka dao,kadau); Malay (sadu, baypay, mambu, veppam); Nepali (neem); Sanskrit (nimba); Sinhala (kohomba); Swahili (mwarubaini, mwarubaini kamili, mkilifi); Tamil (vepa, veppu, veppam, vembu) ; Thai (sadao, kadao, sadao India, khwinin, saliam, cha-tang); Tigrigna (nim); Trade name (neem); Vietnamese (saafu daau, sàu-dàu, s[aaf]u d[aa]u) [1].

1.1.2 BOTANIC DESCRIPTION

Azadirachta indica is a small to medium-sized tree, usually evergreen, up to 15 (30 max.) m tall, with a round, large crown up to 10 (20 max.) m in diameter; branches spreading; bole branchless for up to 7.5 m, up to 90 cm in diameter, sometimes fluted at base; bark moderately thick, with small, scattered tubercles, deeply fissured and flaking in old trees, dark grey outside and reddish inside, with colourless, sticky foetid sap.

Leaves alternate, crowded near the end of branches, simply pinnate, 20-40 cm long, exstipulate, light green, with 2 pairs of glands at the base, otherwise glabrous; petiole 2-7 cm long, subglabrous; rachis channelled above; leaflets 8-

19, very short petioluled, alternate proximally and more or less opposite distally, ovate to lanceolate, sometimes falcate (min. 2)

Inflorescence 3.5-10 x 1.2-4 cm, glossy, serrate; apex acuminate; base unequal an axillary, many-flowered thyrsus, up to 30 cm long; bracts minute and caducous; flowers bisexual or male on same tree, actinomorphic, small, pentamerous, white or pale yellow, slightly sweet scented; calyx lobes imbricate, broadly ovate and thin, puberulous inside; petals free, imbricate, spathulate, spreading, ciliolate inside.

Fruit 1 (max. 2)-seeded drupe, ellipsoidal, 1-2 cm long, greenish, greenish yellow to yellow or purple when ripe; exocarp thin, mesocarp pulpy, endocarp cartilaginous; seed ovoid or spherical; apex pointed; testa thin, composed of a shell and a kernel (sometimes 2 or 3 kernels), each about half of the seed's weight. [1].

1.1.3 BIOLOGY

A. indica trees may start flowering and fruiting at the age of 4-5 years, but economic quantities of seed are produced only after 10-12 years.

Pollination is by insects such as honeybees. Certain isolated trees do not set fruit, suggesting the occurrence of self-incompatibility. The flowering and fruiting seasons largely depend on location and habitat. In Thailand for instance, neem flowers and fruits throughout the year whereas in East Africa (with pronounced dry and wet season) flowering and fruiting are restricted to distinct periods. Fruits ripen in about 12 weeks fromanthesis [1].

1.1.4 ECOLOGY

indica is said to grow ‘almost anywhere’ in the lowland tropics. Under natural conditions, it does not grow gregariously.

In India, it is present in mixed forest with Acacia spp. and Dalbergia sissoo; in Indonesia, it is naturalized in lowland monsoon forest. In Africa, it is found in evergreen forest and in dry deciduous forest. Adult A. indica tolerates some frost, but seedlings are more sensitive. It quickly dies in waterlogged soils. A. indica requires large amounts of light, but it tolerates fairly heavy shade during the 1st few years.

1.1.5BIOPHYSICAL LIMIT

Altitude: 0-1500 m, Mean annual temperature: Up to 40 deg. C, Mean annual rainfall: 400-1200 mm.

Soil type: It grows on a wide variety of neutral to alkaline soils but performs better than most species on shallow, stony, sandy soils, or in places where there is a hard calcareous or clay pan not far below the surface. It grows best on soils with a PH of 6.2-7 [1].

1.1.6 Scientific Classification

The neem tree has been described as A-indica as early as 1830 by De Jussieu and its Taxonomic position is as following [2].

Order	Rutales
Suborder	Rutinae
Family	Meliaceae
Subfamily	Melioideae
Tribe	Melieae
Genus	Azadirachta
Species	Indica

1.1.7 Biological activities and medicinal properties of *NEEM*

Azadirachta indica is perhaps the most useful traditional medicinal plant in India. Each part of the neem tree has some medicinal property and is thus commercially exploitable. During the last five decades, apart from the chemistry of the neem compounds, considerable progress has been achieved regarding the biological activity and medicinal applications of neem. It is now considered as a valuable source of unique natural products for development of medicines against various diseases and also for the development of industrial products.

***Biological activity of some neem compounds**

Although a large number of compounds have been isolated from various parts of neem, a few of them have been studied for biological activity as shown in Table 1.

Neem compound	Source	Biological activity	Reference
Nimbidin	***Seed oil***	-inflammatory Antiarthritic Antipyretic Hypoglycaemic Antigastric ulcer Spermicidal Antifungal Antibacterial Diuretic	***4*** ***5*** ***6*** ***7*** ***8,10*** ***11*** ***12*** ***12*** ***13***
Nimbin	Seed oil	Spermicidal	***10***
Nimbolide	Seed oil	Antibacterial Antimalarial	***14,15*** ***16***
Gedunin	Seed oil	Antifungal Antimalarial	***17*** ***15***
Azadirachtin	Seed	Antimalarial	***18***
Mahmoodin	Seed oil	Antibacteria	***3***
Gallic acid epicatechin and catechin	Bark	Anti-inflammatory and Immunomodulatory	19
Margolone margolonone and isomargolonone	Bark	Antibacterial	***20***
Cyclic trisulphide and cyclic tetrasulphide	Leaf	Antifungal	***21***
Polysaccharides GIa , GIb	Bark	Antitumour	***23***
Polysaccharides GIIa , GIIIa	Bark	Anti-inflammatory	***24***
NB-II peptidoglycan	Bark	Immunomodulatory	***25,26***

1.1.8 PRODUCTS OF NEEM

1- Food: Fruits are eaten fresh or cooked, or prepared as a dessert or lemonade-type drink. The young twigs and flowers are occasionally consumed as vegetables [1].

2- Fodder: The leaves, though very bitter, are used as a dry season fodder. A. indica fruit is an important source of food for some wild life, especially birds and bats ,although they digest only the pulp, not the seed[1].

3- Fuel: Charcoal made from A. indica wood is of excellent quality and the wood has long been used as firewood. Its oil is burned in lamps throughout India [1].

4- Gum or resin: An exudate can be tapped from the trunk by wounding the bark. This high-protein material has potential as food additive and is widely used in southeast Asia as "neem glue" [1].
5- Tannin or dyestuff: Tree bark contains 12-14% tannins. This compares favourably with conventional tannin chemicals [1].
6- Lipids: A. indica oil has long been produced in Asia on an industrial scale for soaps, cosmetics, pharmaceuticals and other non-edible products [1].
7- Poison: Azadirachtin has been identified as A. indica's principal active compound. Extracts can be made from leaves and other tissues, but the seeds contain the highest concentrations of the compound. In India, some Neem-based pesticides include Azadi, Fortune Azadi, Godrej Achook, Margocide, Neemarin, Repelin and Nimbecidine [1]
8- Medicine: Neem has proved effective against certain fungi that infect humans. In a laboratory study, neem preparations showed toxicity to cultures of 14 common fungi. The tree has suppressed several species of pathogenic bacteria, including Salmonella typhosa and Staphylococus aureus. Various parts of A. indica have anthelmintic, antiperiodic, antiseptic, diuretic and purgative actions, and are also used to treat boils, pimples, eye diseases, hepatitis, leprosy, rheumatism, scrofula, ringworm and ulcers. Leaf teas are used to treat malaria. People use the twigs as toothbrushes, and dentists find twigs effective in preventing periodontal disease [1].
9- NEEM OIL:

   Neem seed is a part of Neem tree which has high concentration of oil. Neem oil is widely used as insecticides, lubricant, drugs for variety of diseases such as iabetes and tuberculosis [26] [27]. This oil could also prolong leather goods when it is applied on them [26].

   There are several methods to obtain Neem oil from the seeds like mechanical pressing, supercritical fluid extraction, and solvent extraction

[26]. Mechanical extraction is the most widely used method to extract Neem oil from Neem seed. However, the oil produced with this method usually has a low price, since it turbid and contains a significant amount of water and metals contents. Extraction using supercritical fluid, the oil produced has very high purity; however the operating and investment cost is high. Extraction using solvent has several advantages. It gives higher yield and less turbid oil than mechanical extraction, and relative low operating cost compared with supercritical fluid ***extraction.***

Neem oil, as an organic material, contains several organic compounds such as nimbin, nimbidin, salannin, etc. Since Neem oil is an organic material, it readily dissolved in organic solvents like n-hexane and ethanol.

9-1 Biodiesel:

Biodiesel production is a valuable process which needs a continued study and optimization process because of its environmentally advantageous attributes and its renewable nature. In India Neem tree is a widely grown crop, termed as Divine Tree due to its wide relevance in many areas of study. The present study is intended to consider aspects related to the feasibility of the production of biodiesel from neem oil. This report deals with biodiesel obtained from neem oil which are mono esters produced using transesterification process. The optimum conditions to achieve maximum yield of biodiesel were investigated at different temperatures and with different molar ratio of neem oil and methanol. The temperature increases yield of methyl ester at 55 ^{0}C and a molar ratio of 1:12 were found to be beneficial. From the obtained results it was apparent that the produced biodiesel fuel was within the recommended standards of biodiesel fuel. The fuel properties of biodiesel including kinematic viscosity and acid value were examined. The engine power and pollutant emissions characteristics under different biodiesel percentages were also

studied. Experiments demonstrated that the biodiesel produced using neem oil could reduce smoke and Carbon monoxide emissions, significantly while the Nitrogen oxide emission changed slightly. Thus, the ester of this oil can be used as environment friendly alternative fuel for diesel engine ***[***28***]***

CHAPTER TWO

Expremintal

2. Expremintal

2.1 Chemicals

Sodium hydroxide was obtained from PELLETS Lab tech Chemicals .Methanol was obtained from LOBA Chemiec Pvt.ltd 107.Wode house Road ,Mumbai 400005 India . Sulphuric acid was obtained from (abt.98%)s d fine.cn E M LiMited 315.317, T.V. Industrial Estae , 248, Wovli Road, Mumbai-30.Ethanol was obtained from SHAM LAB .

2.2 Solvents

Chloroform was obtained from ROMIL-SA "select – assured ",and cyclohexane obtained from CDH laboratory reagent.

2.3 Thin Layer Chromatography (TLC)

Thin layer chromatography was carried out using silica gel precoated glasses slide with mobile phase (9.8 chloroform :0.2 ethanol),spots were visualized with Iodine

2.4 Infra Red(IR) spectrophotometer

Infrared spectra were recorded on Thremo Nicolet 300 ,USA

2.5 Ultra Violt (UV) Spectrophotometer

UV spectra were recorded on JENWAY, 6505UV/Vis, British.

2.6 General Equipments

* All glassware of borosilicate
* Electronic balance (SHIMADZU PHILIPPINES MANUFACTURING)
* Soxthelt
* Rotary Evaporator (Stuart)
* Magnetic Stirrer hotplate (Sturat)

2.7 Methods

2.7.1 Sampling

Neem seeds was collected from many Trees at air port area on Atbara Town .it was dried on shadow for Two days then seeds was un wrapping and milled

2.7.2 Oil extraction

100 g of crunched seeds was placed in a thimble of Soxhlet and run it using cyclohexane as a solvent .The mixture of oil and solvent was evaporated in rotary evaporator, 130ml of sample was collected.

2.7.3 Determination of free fatty acid

1ml of oil sample was placed in conical flask, 10 ml of isopropyl alcohol was added ,and the mixture was titrated againest sodium hydroxide (.001m)using phenolphthalein as indicator .

2.7.4 Esterification of oil

100ml of oil was dried at 120℃ on stirrer. 20ml of methanol and 0.2ml of sulfuric acid was added , and let the mixture stirring at 55^0C for one hour .then let it separated for 24 hour.

Using separating funnel biodiesel separated , then it was washed tell the soap completely removed .

CHAPTER THREE

Results and Disscution

3. Results and Disscution

Table 1: Infrared data of biodiesel

C-H Sp3(aliphatic)	C-O St.vib	C=O St.vib	C-C St.vib
2925-2856	1170	1743	721

Table 2:UVdata of biodiesel

Solvent	ג max,nm
n-hexane	450

Table 3: Physical Properties

Density	20 g/cm^3
Viscosity	11.38 mm^2/s
Flash Point	164^0C

Discussion

Neem oil was extracted from neem seeds using soxhlet extractor and cyclohexane as a solvent .The extracting percent found to be 26% , the reported percent was 34%, this variation comes from sample preparation and extraction condition .

IR spectrum shows the peak at 2925, 2856 due to c-H" aliphatic", 1743 due to C=O, 1170 due to C-O and 721 due to "C-C". This indicated the presence of ester.

UV spectrum gave the value of ƛ max which show three electronic transmission($\pi \rightarrow \pi^*, n \rightarrow \pi^*, n \rightarrow \delta^*$) which were found in ester group.

The TLC show that one spot of the product, which indicated that the sample is pure or the solvent is not suitable .

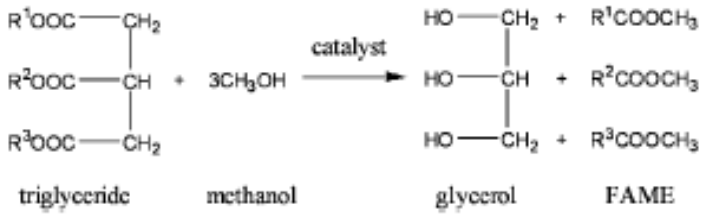
Standard biodiesel show the numbers (3.5-5 mm^2/s), (0.86 -0.9 g/cm^3) and (>101^0C) for viscosity, density and flash point .When our biodiesel show (11mm^2/s), (20 g/cm^3) and (146^0C) .The high increases in all this properties belong to the high molecular weight ,and this indicate the presence of some components with it .Which mean that the sample is not pure.

Conclusion and Recommendation

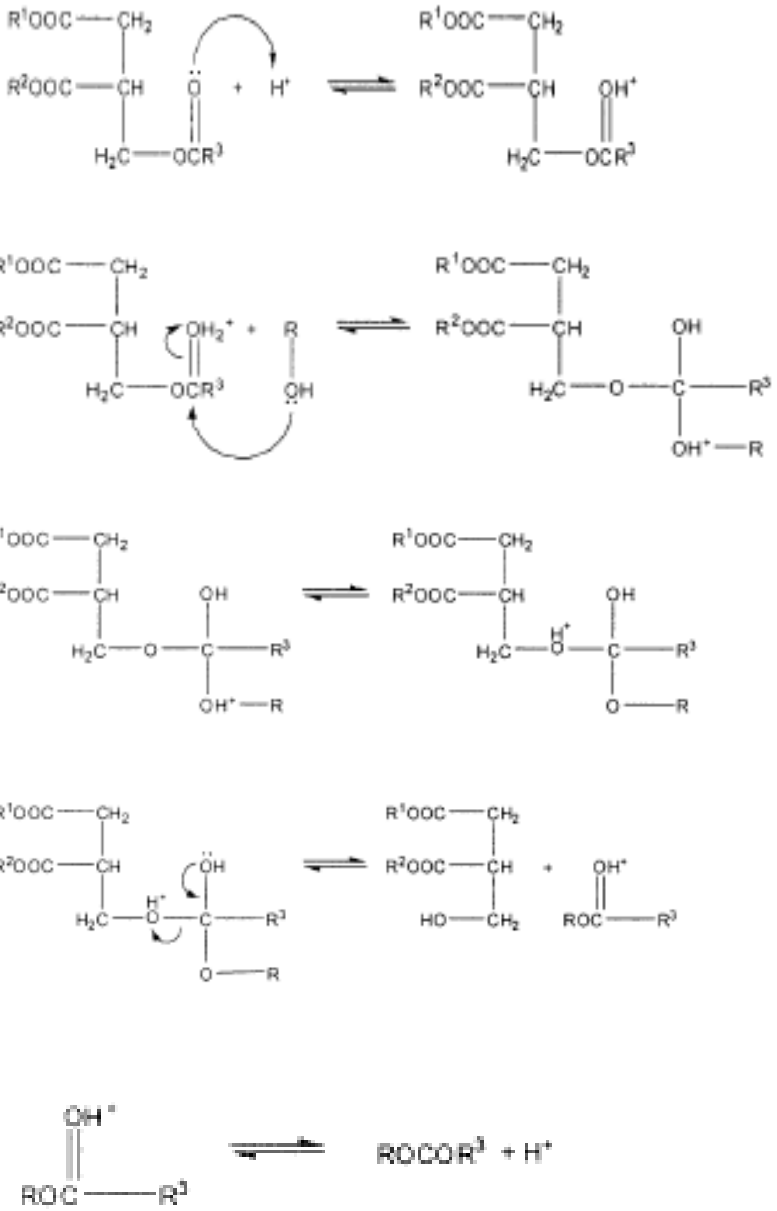
Over this research we enables to transform neem oil into biodiesel by esterification processes and it gave goodish results.

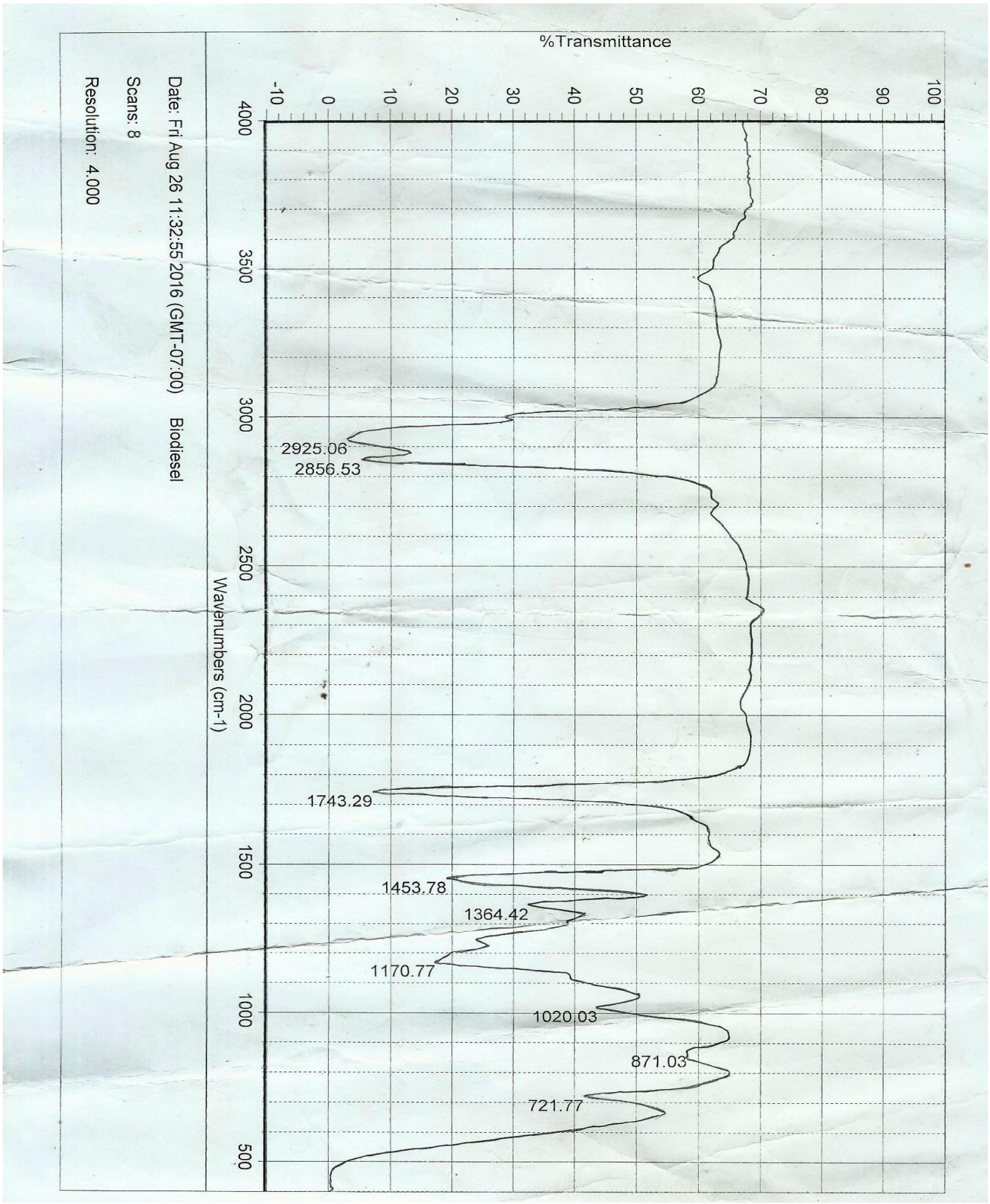
We recommends using an other techniques for separation and structural elucidation such as NMR and mass spectroscopy.

General reaction of esterification



Mechanism of reaction




%Transmittance
-10
0
10
20
30
40
50
60
70
80
90
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
2925.06
2856.53
1743.29
1453.78
1364.42
1170.77
1020.03
871.03
721.77
Date: Fri Aug 26 11:32:55 2016 (GMT-07:00) Biodiesel
Scans: 8
Resolution: 4.000

IR Spectrum

Neem seeds

Dry seeds kernels

Soxhlet extractor

Biodiesel sample on magnatic stirrer

Reference:

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