Study of Tucumã (*Astrocaryum aculeatum*) waste to produce biodiesel by conjugated processes

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Research Article

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Abstract

Transforming waste material into a value-added product has been a challenge in several aspects, legal, academic, economic, and environmental. Tucumã is a fruit widely consumed by the people of the Amazon region, offering this alternative for using the waste generated by it is to provide a source of income for tucumã producers in the northern region of Brazil. To obtain results on yields and reactions that transform tucumã waste into biodiesel, first the seed oil was extracted by decoction, followed by conjugated process. The thermal cracking reaction, produced smaller chains than the raw material, followed by the esterification reaction applying heterogeneous catalysis using aluminum oxide. These processes transform the tucumã waste into esters similar to biodiesel compounds, the products were characterized by techniques such as gas chromatography coupled to mass spectrometry (GCMS) and Fourier transform infrared spectroscopy (FTIR), achieving a yield in the conversion of tucumã seed oil into methyl esters (biodiesel), above 90%, in addition, we reached specific mass parameters of 863 Kg/m^3 and viscosity of 4.3 mm^2/s, data that allow us to affirm that the application of conjugated reactions of this material as fuel meets the product specifications, providing added value. The data generated in this work will make it possible to open space for the studies of these processes on a pilot scale, which will enable local energy autonomy regarding the use of biodiesel.

Introduction

Astrocaryum aculeatum is a palm tree native to the Amazon Forest that occurs in northern Bolivia, the Colombian Amazon, Venezuela, Guyana, Suriname, and Brazil, throughout the western Amazon to western Pará, Mato Grosso, and Roraima. [1] The pulp contains a high content of pro-vitamin A (carotene, 51.000 international units – IU/100 g), lipids and energy, and an average content of β-carotene. [2] It stands out for its contents of potassium (K) (1396.02 mg/100 g) and selenium (Se) (9.32 μg/100 g). In 100 g, it has moisture (38.5%), protein (5.5%), ash (2%), lipids (47.2%), total dietary fiber (19.2%), carbohydrates (6.8%) and energy (474 kcal). [3] The exploitation of tucumã pulp and its derivatives represents significant and growing economic activity at the regional level. The orange pulp of tucumã is in the daily life of Amazonians and is consumed in natura in local cuisine, such as sandwiches, bread, and creams. [4]

Sales and extractivism activities in Manaus are not related to entrepreneurship,[5] as it is a regional fruit of forest origin, it is rarely sold in supermarkets, but it is abundant in marketplaces and strategic points of sale in the streets of Manaus, where it can be found throughout the year. [6] However, although permanent, the supply of fruit throughout the year is heterogeneous, which determines a variation in its price. The fruit is commonly marketed in two ways: in nature, sold by the dozen or by the hundred, and locally processed by the traders themselves, with the pulp being sold by weight. In January 2012, of the 41 marketplaces registered with the Municipal Department of Production and Supply (SEMPAB), regular tucumã traders have identified some marketplaces: (I) Municipal Producer Fair from the East Zone; (II) Dorval Porto Municipal Market; (III) Municipal Fair of Park 10; (IV) Panair Municipal Fair; (V) Adolpho

Lisboa Municipal Market; and (VI) Walter Rayol Municipal Market, concluding that the Manaus market is served almost exclusively by extractive exploration, which implies the absence of more consistent official data regarding consumption and waste generated by this trade. [7] Approximately 367.8 tons of tucumã were sold in the period 2011/2012, which states that 83 tons were sold monthly in 2017, with the same value forecast for 2018 and subsequent years. [3,5–7] However, because of the COVID-19 pandemic, we did not consolidate quantitative and solid information on the increase in tucumã sales. The isolation measures, in a way, did not allow us to go to the marketplaces to measure these data from 2020 to 2022. However, we can say that the data until 2018 and 2019 show a significant increase in the supply of fruit and, consequently, in the amount of fruit and discarded waste.

The destination of the waste after consumption of the tucumã fruit pulp is an important indicator for the evaluation of the reuse potential, since approximately 61.3% of the fruit refers to the woody endocarp, so it is necessary to use them for the manufacture of eco-friendly marketable products, such as wood-plastic derivatives and eco composites. Approximately 91.9% of the seeds are discarded in the trash, without reuse, 2.3% for crafts (buttons, rings), 2.3% are used for planting the fruit, 1.2% for raising animals, 1.2% for sale, and 1.2% for donation. [7] There is a low potential for the reuse of tucumã seeds. The almonds discarded together with the seeds have great potential, and the almonds can be roasted and ground and used to make tucumã coffee and for oil extraction. [3] The tucumã almond is an Amazonian oilseed species that meet the fundamental criteria for adequate and sustainable use for the production of biodiesel in the Amazon[8]. Laboratory tests showed that it is possible to run a generator with biodiesel from tucumã.[9]

The feasibility of obtaining biodiesel as an alternative source of energy depends on several factors, including the composition of the raw material or the biomass. Many studies have been developed using biomass or waste, such as waste factors [10][11] and vegetable oil[12], even to transform vegetable oils into hydrocarbons similar to diesel oil,[13] and many processes have been applied to transform biomass into energy[14]. From these characteristics, conjugated processes were studied, to produce solid data that allow the elaboration of processes on a pilot scale to supply the local vessels themselves.

Materials And Methods

The seeds, tucumã wastes, were collected from the “marketplace of bananas”, and at Manaus Moderna Market, approximately 20 kg of waste was collected. Regarding the reagents and solvents, all were obtained on an analytical scale from the company VETEC Química Fina LTDA and used in the form in which they were acquired.

General Procedures

Treatment and preparation of tucumã seeds

The definition of these steps is very important because one of the reasons raised in our research for not using the seed or even the hard and woody lump is the difficulty of breaking this lump. The collected tucumã stones were transported to the laboratory, where they underwent a washing process to remove surface dirt and sanitization with sodium hypochlorite. After this cleaning, it were separated for the processing of removing the seed from the woody endocarp (stone), where four processes were tested, three in the first phase of the project and one in the second. *1st Process:* Removal of the Tucumã seeds with Drying. The stones were subjected to a temperature of 121 °C at a pressure of (1 atm, relative pressure) for 1 h in autoclave equipment, distributed homogeneously in trays, and then subjected to the drying process at a temperature of 75 °C/24 h in a PID digital sterilization and drying oven (BIOPAR). After drying, the tucumã stones were manually broken with the aid of a pressure machine (Kelly button punch, n° 5) obtained the seeds. *2nd Process:* Removal of the seeds from Tucumã without drying. The stones were submitted to a temperature of 121 °C at a pressure of (1 atm, relative pressure) for 1 h in autoclave equipment and then, the stones was manually broken with the aid of a pressure machine (Kelly button punch, n° 5). *3rd Process:* Removal of the Tucumã seeds with freezing. The stones were frozen at approximately -6 °C and then kept at a temperature of 121 °C with a pressure of 1 atm (relative pressure) for 1 h in autoclave equipment. The tucumã seeds were manually broken with the aid of a press machine (Kelly button punch, n° 5. *4th Process:* Removal of the seeds from Tucumã with a Pressure Cooker. The stones were subjected to freezing at approximately -6 °C and placed in a pressure cooker for 1 h on high heat. The tucumã stones were manually broken with the aid of a hammer. At the end of all processes, the seeds were ground in TECNAL's R-TE-651 rotor mill.

Tucumã seed oil extraction process

The extraction processes were performed in two ways: solvent extraction in Soxhlet with PA hexane and decoction. Solvent extraction was carried out by weighing 5 g of ground alcohol with enough hexane to carry out the extraction. Afterward, the seed oil was dried in a rotary evaporator, and the extracted oil was weighed, calculating the yield of this process. The extraction of oil by decoction was carried out by weighing approximately 200 g of crushed almond, and weighing procedures were carried out until approximately 1 L of oil was extracted from the almond, which was placed in the cooking process at a temperature of approximately 100 °C, for 1 h, after which the oil was separated in a funnel and then passed through the rotary evaporator. The final oil was weighed to calculate the yield.

Fuel Upgrading

Transesterification reaction

The transesterification reaction was carried out at room temperature for 2 h, and 150 g of almond oil, 600 g of methanol, and 15 g of KOH were reacted. [17]

Thermal Cracking reaction

For the thermal cracking reaction, 250 g of tucumã seed oil was weighed in a three-neck flask coupled to a condenser and a collector flask and heated to a temperature of 380 °C for 1 h. The product was filtered and dried on a rotary evaporator.

[15,16,17]

Esterification reaction

For the esterification reaction, 100 g of the product of the cracking reaction was weighed, 85 g of methanol PA and 0.3 g of aluminum oxide as a catalyst were added, and everything was mixed in a single-mouth flask coupled to a condenser on a heating plate with magnetic stirring at a temperature of 180 °C for 1 h of reaction. After the reaction, the product was centrifuged, and the catalyst was removed and dried on a rotary evaporator to remove residual methanol and water. [16,17]

Physico-chemical procedures

It was also determined the main physical-chemical properties of the biodiesel from tucumã waste, using standard methods: density (ASTM D 442), ash content (ASTM D 482), kinetic viscosity (ASTM D 445), acid value (AOCS Cd 3d-63), and flash point (ASTM D 93).

Liquid Products Characterization

The results were analyzed by techniques such as gas chromatography (GC─MS) performed in the equipment Agilent Technologies - Model CG-7890B coupled to a Mass Spectrometer model MS-5977A, fused silica capillary column SLBTM-5ms (30 mx 0.25 mm x 0.25 um). Data processing was performed in the Data Analysis software and from the interpretation of the chromatograms and the identification of the compound according to the library of mass spectra of the National Institute of Standards and Technology (NIST). Infrared (IR) spectroscopy was performed on a Shimadzu FTIR spectrophotometer (model IRAffinity-1S) with an ATR8000 accessory coupled with a scanning range from 400 to 4500 cm-1. To study the yield of the reactions, the analysis of the acidity index was carried out by the AOCS 3d-63 method. [16,17]

Results

Definition of the seed extraction process

The definition of the process of removing the seeds from the stones waste, the tucumã endocarp, deserves to be highlighted because as it is a proposal for the use of the residue, we need to emphasize the characteristics of the residues as they are found. The hard wrapping that covers the seed is difficult to handle because it has a thick shell and is very hard to break, which is also one of the reasons why its use is not popularly applied. Thus, four processes were tested to remove the whole seed. In **Fig 1,** we present some details of the processes tested. After this process of removing the almond, they were all crushed and subjected to the oil extraction process.

About seed oil, the solvent extraction showed a yield of approximately 88 %, but it became an expensive process when compared to the decoction process, which showed a yield of 91 %. Therefore, it was decided to analyze the oil obtained by the decoction process.

Characterization of seed oil of tucumã

The oil extracted both by solvent and by cooking showed a solid consistency at room temperature. After the transesterification reaction, it presented a liquid consistency. Initially, the base oil was characterized by GC–MS and FTIR, and the acidity was analyzed, which presented a value of 23.83 mg KOH/g sample. After the transesterification reaction was performed, the oil presented a pasty consistency. **Fig 2** shows the chromatogram of the transesterified *tucumã* seed oil, where it is suggested that its composition be, according to analysis compatibility (NIST), those described in peaks 1 to 5, and the main peaks were identified by mass spectrometry and are presented in **Table 1.** It is noted that the oil is mainly composed of saturated chain carbons ranging from C9 to C15 (compounds with higher peaks), which justifies the pasty consistency mentioned at the beginning. It is possible to identify that the most intense peak is 3, which has a C13 chain. FTIR analysis of the tucumã seed oil was also performed, where the composition of the carbonyl bonding band (C = O) present in esters was identified at 1740 cm^{-1} and identified in the spectrum of **Fig 3.**

Table 1 The main peaks identified by mass spectrometry of seed oil of tucumã

Point	Ret. time	MF	MM	Nomenclature
1	18.306	$C_9H_{18}O_2$	158	Octanoic acid methyl ester
2	23.267	$C_{11}H_{22}O_2$	186	Decanoic acid methyl ester
3	28.314	$C_{13}H_{26}O_2$	214	Methyl ester of dodecanoic acid
4	32.948	$C_{15}H_{30}O_2$	242	Methyltetradecanoate

Thermal cracking reaction – Fuel upgrading

Due to its degree of acidity and saturated chain compounds, the study of the application of conjugate processes was developed, starting with the thermal cracking reaction. The reaction product showed an acidity of 166 mg KOH/g sample, which by GCMS identification analysis suggests that this is due to the presence of dodecanoic acid, identified at peak 4 of the chromatogram of **Fig. 3.** The peaks are identified from 1 to 9 with chains formed from C9 to C19 (**Table 2)**. In addition to the FTIR analysis, as well as the acidity index, it is noted that there is an intense band corresponding to the C = O bond present in the fatty acids at 1710 cm^{-1} according to the spectrum shown in **Fig. 4.** The product of this reaction no longer has a viscous appearance at room temperature, thus more closely resembling the characteristics of biodiesel.

Table 2 The main peaks identified by mass spectrometry of seed oil of tucumã from the cracking reaction

Point	Ret. time	MF	MM	Nomenclature
1	25.090	$C_9H_{18}O_2$	158	Methyl octanoic acid ester
2	31.727	$C_{11}H_{22}O_2$	186	Decanoic acid methyl ester
3	37.459	$C_{13}H_{26}O_2$	214	Methyl ester of dodecanoic acid
4	38.445	$C_{12}H_{24}O_2$	200	dodecanoic acid
5	42.737	$C_{15}H_{30}O_2$	242	Methyl tetradecanoate
6	47.491	$C_{17}H_{34}O_2$	270	Methyl ester of hexadecanoic acid
7	51.862	$C_{19}H_{34}O_2$	294	Methyl ester of 9,12-octadecenoic acid
8	52.013	$C_{19}H_{36}O_2$	296	Methyl ester of 9 – octadecenoic acid
9	52.769	$C_{19}H_{38}O_2$	298	Methyl stearate

Esterification reaction – Fuel upgrading

To reduce the acidity content of the material and make its application as a biofuel possible, the esterification reaction was performed and presented an acidity value of 13.85 mg KOH/g sample, giving a yield of 91.66 % inthe conversion of acidity to esters. **Fig. 5** shows the esterification reaction product chromatogram. The suggested composition follows the esterification reaction pattern with methanol and methyl esters ranging from C11 to C19 (**Table 3**) but without the presence of fatty acid peaks. The products of the esterification reaction presented compounds that can be apply into blends of diesel oil and biodiesel.

Table 3 The main peaks identified by mass spectrometry of seed oil of tucumã of the esterification reaction

Point	Ret. time	MF	MM	Nomenclature
1	31.718	$C_{11}H_{22}O_2$	186	Decanoic acid methyl ester
2	37.567	$C_{13}H_{26}O_2$	214	Methyl ester of dodecanoic acid
3	42.739	$C_{15}H_{30}O_2$	242	Methyltetradecanoate
4	47.460	$C_{17}H_{34}O_2$	270	Methyl ester of hexadecanoic acid
5	52.070	$C_{19}H_{34}O_2$	294	Methyl ester of 9,12-octadienoic acid
6	52.686	$C_{19}H_{36}O_2$	296	Methyl ester of 9 – octadienoic acid

Following to confirm that there was the removal or significant reduction of acidic compounds to obtain biodiesel from the tucumã oil, FTIR analysis was performed, in which the spectrum of the esterification reaction product is presented. **Fig. 6** shows the presence of the band seen at 1740 cm^{-1} and the output of the band referring to the presence of fatty acids at 1710 cm^{-1}

Finally to define the quality of the product, the data of density, viscosity, flash point and ash content are presented in the **Table 4.** all parameters analyzed in relation to the final product were within the admissible values for its application as biodiesel.

Table 4 Physico-chemical parameters

Parameters	Reference value	Results
Density	800-900 (kg/m^3)	863
ash content	0,020 (% mass)	0,01
kinetic viscosity	3,0-6,0 (mm^2/s)	4,3
flash point	min 100 ºC	120

Conclusions

The results of conjugated processes to produce biodiesel using waste of tucumã, were promising due to its 91.6% yield and its fatty acid methyl ester composition. The density and viscosity data within the regulated parameters allow us to confirm that the fuel meets the purpose of the research, that is, the use of internal combustion engines that use diesel oil or blends diesel oil x biodiesel, as fuel. The use of *tucumã* waste, a fruit consumed on a large scale in the northern region of Brazil, proved to be effective, and in our proposal, it makes a disposal destination available instead of simple disposal in landfills. For purposes of continuity, our next step is to study the physico-chemical parameters and the application of this biofuel in blends to be tested in IFAM vehicles that use diesel fuel.

Declarations

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Conflicting interests: The authors declare that there are no conflicting interests.

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Figures

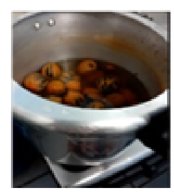
process	Seed coloring	Seed Integrity	observations	Seed appearance after application of the process
1st	They showed a darkened and dry color.	The seeds were adhered to the shell, requiring the removal of the remaining fraction with the use of stainless-steel knives.	The drying process facilitated the removal of the kernels from the woody endocarps.	
2nd	They presented a lighter color (white) than process 1 and dried.	Very adhered to the shell, which made it difficult to remove, leaving fractions of the almond.	This process did not show satisfactory results for production.	
3rd	They presented a whitish and dry color.	Little adhered to the woody endocarp, it facilitated the removal of the integument.	This process showed satisfactory results for the production and obtaining of almonds.	
4th	Unable to remove the almond.	The woody endocarp became very resistant, making it impossible to remove the almond.	This process did not show satisfactory results for production.	

Figure 1

Processes tested to remove the whole seed of tucumã

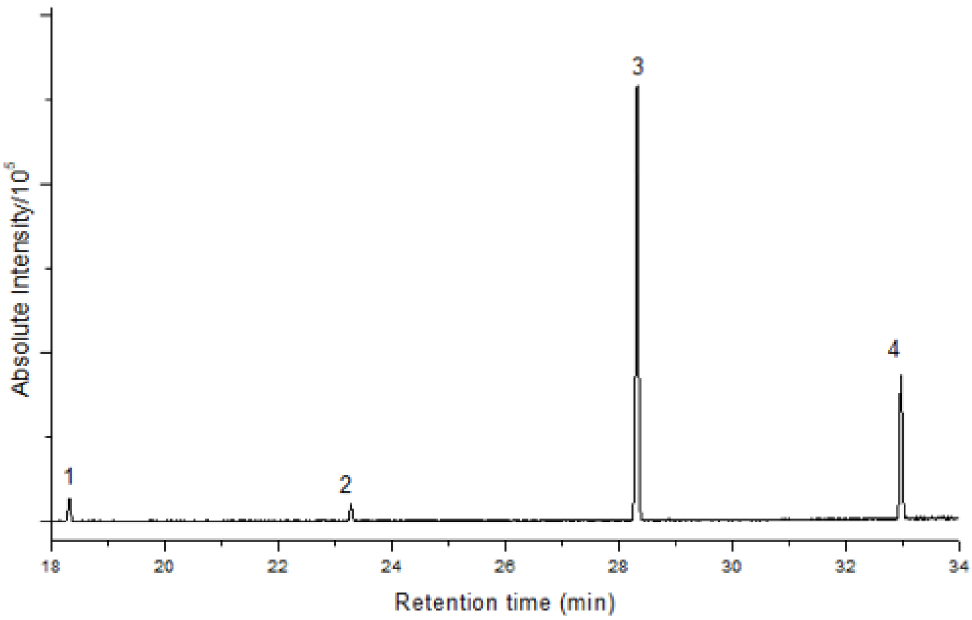


Figure 2

Tucumã seed oil chromatogram.

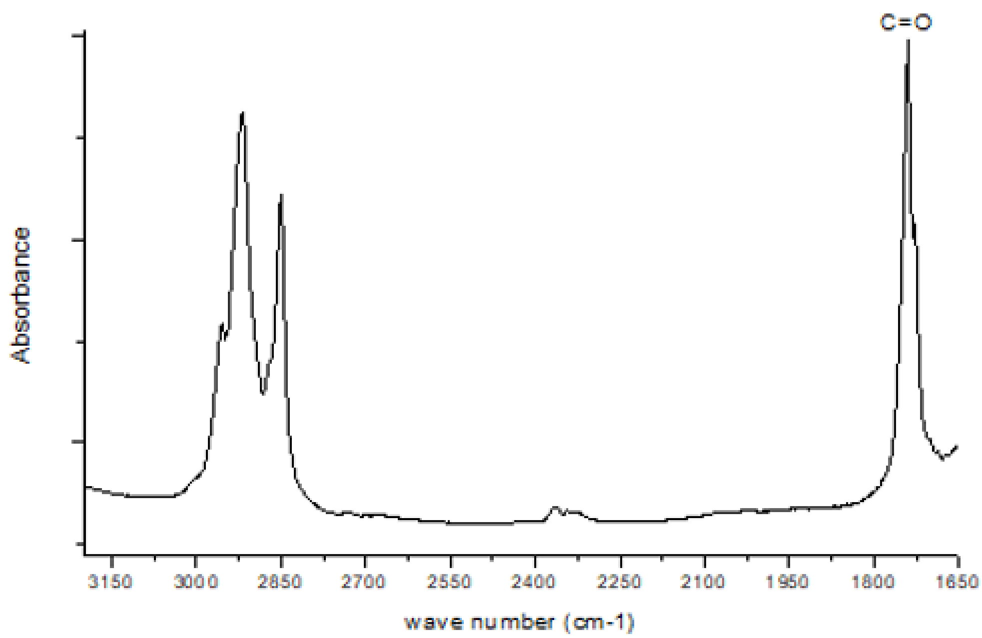


Figure 3

FTIR spectrum of the Tucumã seed oil

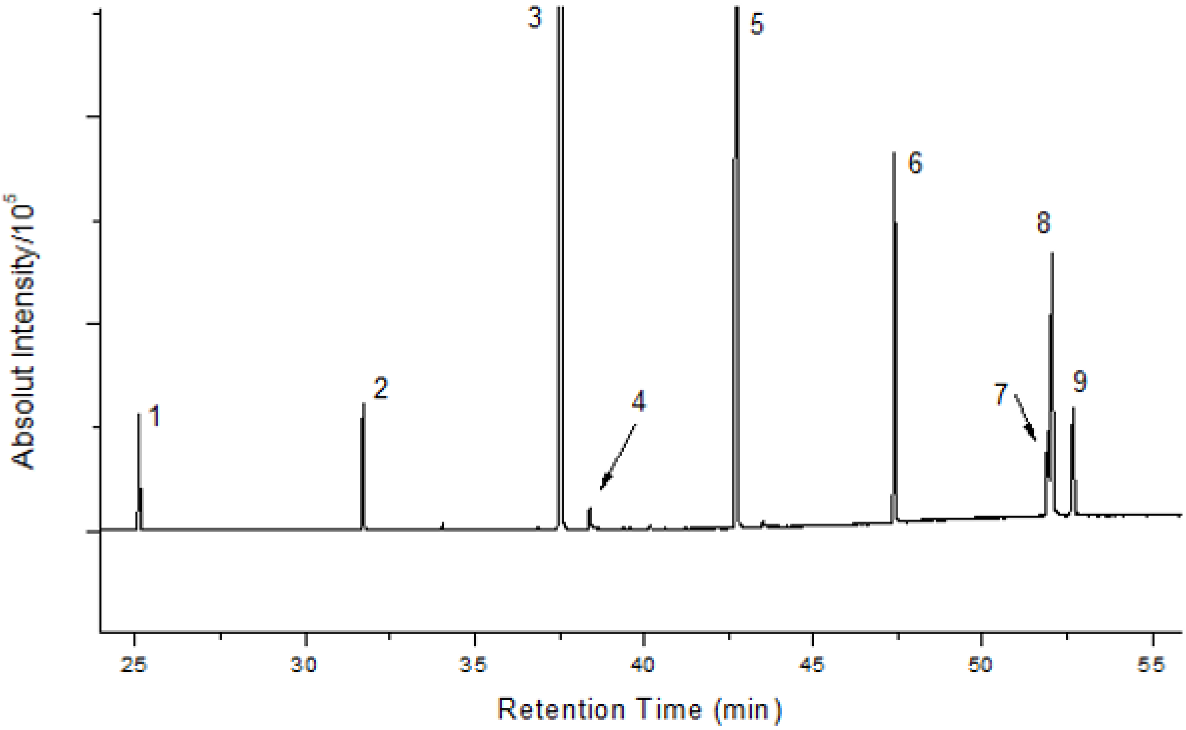


Figure 4

Chromatogram cracking reaction of seed oil

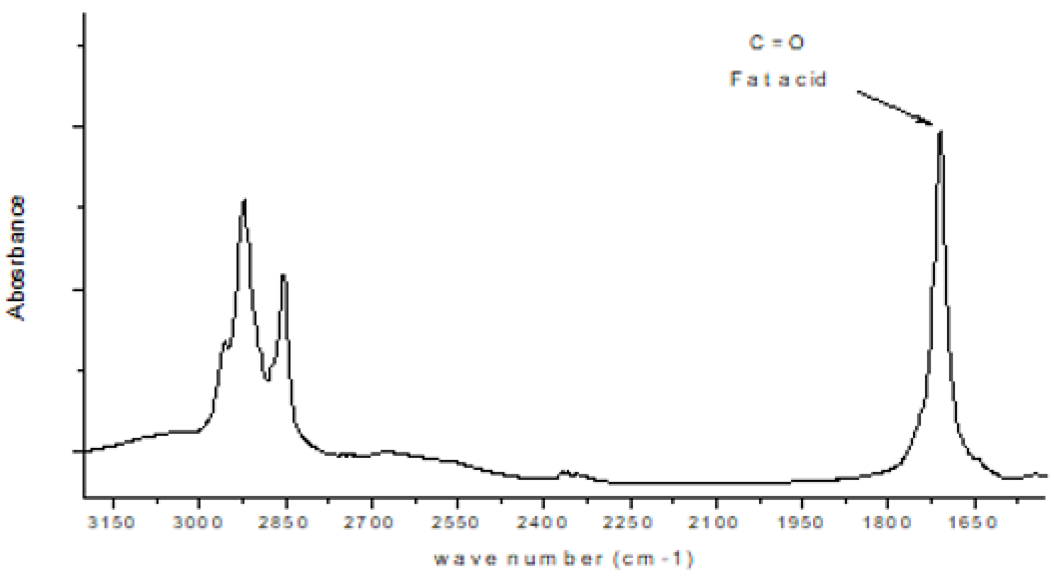


Figure 5

FTIR cracking reaction of seed oil

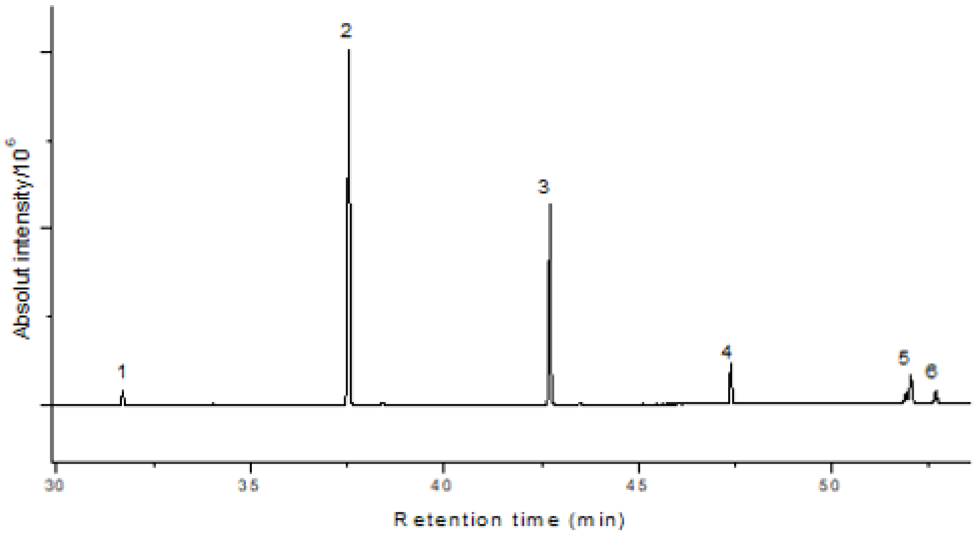


Figure 6

Esterification reaction chromatogram.

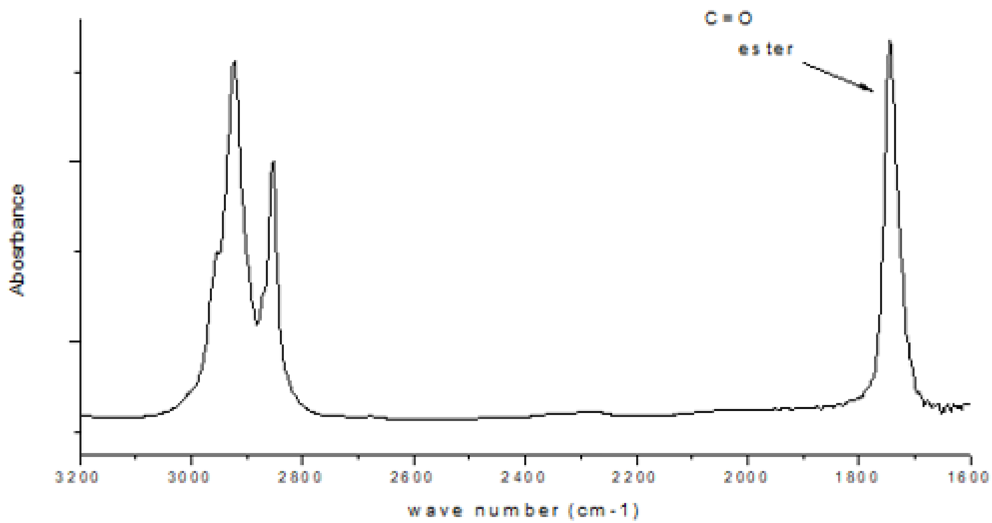


Figure 7

FTIR spectrum of the esterification reaction.