

Effect Of Reaction Temperature On The Total Petroleum Hydrocarbon Of Biodiesel Produced From Waste Cooking Oil Using A Heterogenous Catalyst.

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Abstract

The increasing demand for energy and the consequent fossil fuel reserves has led to the search for alternative fuels which are renewable and sustainable. Biodiesel a renewable fuel has proven to be a suitable alternative in combustion engine compared to the petrodiesel because of its biodegradability and smoother combustibility. Transesterification of waste cooking oil to biodiesel was carried out with methanol to oil molar ratio of 8:1 using activated carbon from coconut shell as catalyst. The temperature of the reaction was varied. The total petroleum hydrocarbon (TPH) of the biodiesel produced were determined at reaction temperatures of 40°C, 50°C and 60°C, while biodiesel properties produced at 40°C, 45°C, 50°C, 55°C and 60°C were also determined. The concentrations of total petroleum hydrocarbon for biodiesel at temperatures of 40°C, 50°C and 60°C were 1652.65, 9629.803 and 9608.752 respectively. Total petroleum hydrocarbon explains the nature of the oil used in the transesterification and hence the quality of the biodiesel produced. Higher temperature above 50°C does not favor the presence of some hydrocarbon in the fuel produced. The properties of the biodiesel produced conform to ASTM D 6751.

1. Introduction

Researchers has developed a wide variety of efficient and novel waste recycling technologies in an effort to recover resources and maximize the transformation of trash into useful components and finished goods [1]. Sustainable industrialization throughout the past decade has been driven by factors such as growing population, new technologies, more generous investment incentives, greater trade and capital liberalization, and new finance sector innovations. Researchers and industrialists face the task of delivering low-cost, environmentally friendly resources that meet modern manufacturing techniques in order to keep up with the increasing demand for raw materials brought on by the current industrial revolution. So, WCO which stands for "waste cooking oil," which refers to used oil and fat from the kitchen. WCOs are commonplace in both commercial and domestic kitchens, especially those serving food. Population growth is causing a rapid increase in the quantity of WCO generated by households and food service establishments [2].

WCO can, however, be converted into biodiesel for use in a variety of applications if it is first catalyzed using a number of different types of agricultural waste [3]. With its low emissions and desirable chemical features like non-toxicity and biodegradability, biodiesel made from renewable resources is one of the most enticing alternative fuels being developed at the moment [4]. Additionally, unlike non-renewable fuel, biodiesel fuel may be used in any standard diesel engine (petroleum or diesel). Aside from being quickly depleted, the nitrogen, sulfur, carbon oxides, lead, and hydrocarbons released during combustion are also negative aspects of using nonrenewable fuel [5]. The optimal production of biodiesel involves the assessment of the amount of total petroleum hydrocarbon (TPH) present at each temperature state, which leads us to the definition of TPH:

Total Petroleum Hydrocarbons, also known as TPH, is used to describe petroleum, often known as crude oil. Petroleum is composed of thousands of distinct components. They contain hydrogen in addition to carbon is what gives them their name: hydrocarbons. The percentage of crude oil that is comprised of petroleum hydrocarbons ranges from fifty to ninety-eight percent, depending on the origin of the petroleum, and is considered an essential component [6]. TPH is released into the environment as a result of industrial releases, oil spill occurrences, or the disposal of waste materials from domestic or commercial use. Oil spills in coastal seas are typically caused by ship operations, tanker collisions, oil exploration, and oil production. Crude oil spills are a frequent occurrence in the oil industry, particularly in offshore drilling, transportation, and transfer. Secondly, the hazardous effluent flow from petroleum refineries is a well-documented contributor to pollution [7]. The amount of oil spills is still a problem for the environment, despite the fact that statistics show a definite declining trend in the frequency of oil spills over the previous 50 years. There have been more than 140 large spills, totaling over 7 million tons of hydrocarbon oil spilled into the environment [8]. An estimated one thousand tons of petroleum hydrocarbon oil will be lost in 2020 owing to tanker spills. It was the same in 2012 and 2019. The list of recent and global oil spills includes over 200 incidents, both on land and at sea. Every year, millions of tons of petroleum are released into the ocean due to both natural seepages and human-caused oil spills [9].

The environmental impact of waste cooking oil disposal and the potential for its reuse as a resource has been of great concern. In contrast, finding a renewable energy source that can replicate the features and components of petro diesel is a problem that needs to be solved. In response, scientists realized they could use waste cooking oil as a feedstock to produce biodiesel. The total petroleum hydrocarbon of the biodiesel produced is the main factor in determining the characteristic grade of this futuristic goldmine obtained from this feat. Thus, it is imperative it be of the best quality standard thereby obtaining the temperature at which the total petroleum content is optimum in order to aid in the production of the best biodiesel.

When food is prepared and fried using edible vegetable oil, a byproduct is waste cooking oil (WCO). WCO is referring to oil used for deep frying, edible fat mixed with kitchen rubbish, or oily wastewater sent directly into sewers. Used vegetable oils and animal fats are readily available worldwide, especially in developed countries. However, the term used or waste cooking oil differs in meaning from person to person but in totality it means an oil that has loosed it frying strength and regarded as trash.

Oils and fats present a significant management challenge due to the evident difficulty of disposing of them and the potential for contamination of water and land resources. The Energy Information Administration estimates that daily generation of spent cooking oil in the United States totals roughly 100 million gallons, or 9 pounds per person [10]

While some of this waste cooking oil is recycled into soap, the vast majority is simply dumped into the environment. Since cities have a bad habit of dumping WCO in sewers, drains, open areas, rivers, and woodlands, where it can generate foul odors, clog drainage pipes, damage concrete, and harm both terrestrial and aquatic ecosystems. Foam formation, an increase in the organic load on water sources, difficulties in wastewater treatment, a decrease in dissolved oxygen levels, and a shift in the equilibrium of the environment are all possible results of improper disposal of WCOs [11]

Due to the similarities between the two countries, it was decided to assume that the annual per capita production of waste cooking oil in Canada is 9 pounds. Statistics Canada estimates that 33 million people currently reside in Canada. Therefore, it is possible that Canada generates about 135,000 tons of used cooking oil annually. An annual output of 700,000-1,000,000 tons of wasted cooking oil was recorded across EU member states [12]. There are around 200,000 tons of discarded cooking oil produced every year in the UK [13]. Reducing environmental contamination caused by the massive amounts of waste cooking oils unlawfully thrown into rivers and landfills is a key benefit of using biodiesel as a Petro diesel alternative made from waste cooking oil [14]. Some solutions have been proposed for dealing with WCO that would lessen their impact on the environment, including better management, disposal, minimization, recycling, conversion, utilization, valorization, and remediation. Utilizing waste cooking oil for biodiesel production could help cut emissions of carbon dioxide, nitrogen oxide, and other pollutants. Most of the carbon in biomass-derived fuel is biogenic and renewable. Used cooking oil is one of the cheapest and most readily available sources for biodiesel production. The cost of feedstock contributes for around 70-80% of the entire cost of manufacturing biofuel, hence WCO has been recognized as a feasible strategy to reduce this cost. WCO is widely available, low-cost, yields a lot of usable product, and doesn't harm the ecosystem. Several technologies have also been developed to chemically and biologically transform WCO into biofuels. Because the cost of feedstock is one of the primary concerns with the process, using waste cooking oil considerably increases the economic sustainability of biodiesel production.

2.0 Methodology

2.1 Esterification of waste cooking oil

500ml of waste cooking oil was measured using the measuring cylinder it was poured into bottom flask and methanol at the 125ml mark quantity were added to the flask at a ratio 1:4. The mixture was kept on the magnetic stirrer for an hour at a steady temperature of 60°C where 1% of H₂SO₄ was added during the rigorous mixing process. After an hour, the mixture was poured into a separating funnel which was kept standing for 24hrs for the separation process to occur. The aim of this process was to reduce the free fatty acid (FFA) in the used cooking oil so as to hinder the formation of soap in the transesterification process to the biodiesel which is the desired end point we are interested in.

2.2 Transesterification of waste cooking oil

The weighing balance was used to measure 55g of the waste cooking oil into the conical flask at the ratio 8:1, which was continuously stirred on the magnetic stirrer with the simultaneous addition of heat. 1g of NaOH was added and 2g of the catalyst was added likewise. From the ratio used, the amount of methanol added was calculated and 16.56g of methanol was added into the conical flask for the transesterification process to occur which yielded the Biodiesel production. The process was repeated at varying temperatures which were at 40°, 45°, 50°, 55°, and 60°

2.3 Preparation of catalyst

During the experiment, the coconut shell was subjected to the carbonization process, and a chemical activation approach was employed. To activate the carbonized coconut shell, phosphoric acid was utilized.

2.3.1 Experimental Procedure

After being sun-dried and then placed in the oven at temperatures between 100 and 300 degrees to eliminate excess moisture, the raw material samples of coconut shells were rinsed with distilled water to remove any inorganic material that might be present. The sample was dried, then broken into smaller pieces in preparation for the carbonization process in the muffle furnace.

2.3.2 Carbonization Process

A horizontal programmable furnace was used to carbonize the raw material sample. The 60.61g shell sample was placed in the center of a quartz boat. Until the target carbonization temperature (500 degrees) was reached, the sample was heated at a steady rate of 6 degree/min using a flowrate of 100 mL /min of nitrogen. It was kept at 500 degrees for an entire hour. Following carbonization, just around 40g remained a reduction of about 34% in mass.

2.3.3 Activation Process

After the carbonization process, char samples were chemically activated using phosphoric acid (H_3PO_4). Impregnation was done using 100 ml of 0.5M solution of phosphoric acid mixed with 30g of the carbonized shell. The mixture was kept soaked for 72hrs to allow for proper activation and then removed from the solution. The activated carbon was washed till neutral with distilled water to remove excess phosphoric acid. It was properly dried in the oven for an hour at 105⁰C which was afterwards taken into the muffle furnace for further activation process aiding the surface area and pore formation.

3.0 Results and Discussion

For the GC analysis, materials were extracted using a modified version of the USEPA 8015 technique for diesel range organics (DRO). The instrument used for the analysis was the HP5890 PLUS II with the detector as flame ionization detector. The composition at various temperatures is displayed in the table below.

Table 1: Total petroleum hydrocarbon concentration at varying temperature

TPH	Concentration(μ g/L)		
	40 ⁰ C	50 ⁰ C	60 ⁰ C
n-octane	<0.01	180.5389	221.8381
n-nonane	101.0506	1.866286	0.209383
n-decane	106.9504	5.364262	143.5602

n-undecane	0.163120	27.51849	<0.01
n-dodecane	637.8479	1374.535	243.0964
n-tridecane	8.603761	0.697638	16.06723
n-tetradecane	8.426814	1187.820	70.37475
n-pentadecane	71.72041	198.9259	235.6981
n-hexadecane	98.02745	2153.429	1633.884
n-heptadecane	81.31296	44.62819	5.444186
Pristane	182.8537	85.18941	39.51925
n-octadecane	175.3982	24.16912	2197.611
Phytane	39.06693	24.97422	8.298555
n-nonadecane	24.08437	504.3024	98.14532
n-eicosane	24.52543	2233.245	2562.736
n-heneicosane	8.148551	453.5538	264.3281
n-docasane	15.56609	991.2703	1636.659
n-tricosane	2.101071	47.02346	23.34783
n-tetracosane	0.343233	<0.01	111.7804
n-pentacosane	0.857689	25.61895	3.288261
n-hexacosane	0.560919	43.64406	12.89782
n-heptacosane	2.901913	4.126324	5.915126
n-octacosane	2.934670	4.126324	5.915126
n-nonacosane	0.587658	9.978404	8.923421
n-tricontane	2.821470	0.818808	1.806131
n- hentriacontane	40.64845	0.646767	1.109832
n-dotriacontane	2.872587	0.254951	5.432951
n-titriacontane	12.27344	4.540271	55.05294
∑ TPH	1652.65	9629.803	9608.752

However, it can be deduced that from the compilation of the data shown in table 1 above, the transesterification process carried out at temperature of 50⁰ C produced the best quality in terms of the amount of total petroleum hydrocarbons present.

Table 2: Physicochemical Properties of Biodiesel from waste cooking oil

Temperature(°C)	Flash point	pH	Density (g/ml)	Acid Value(mgKOH/g)	Viscosity
40	-----	6.70	870	0.672	-----
45	-----	6.52	879	0.543	-----
50	142.5	6.86	890	0.562	4.43
55	-----	6.62	882	0.520	-----
60	-----	6.70	891	0.690	-----
ASTM D6751	130 min	6.5-6.8	880-890	0.5-0.6	1.9-6.0

The diesel range organics that were produced by the biodiesel ranged from n-octane to ntriacontane (C₈ - C₃₃). These diesel organics are the essential defining qualities of the biodiesel produced. It was observed that the functional group largely represented was the alkane group, having various petroleum hydrocarbons being present. Also, due to their primary presence in crude oil, pristane and phytane are considered to be one of the most important constituents which gives a proper overview of the source of biodiesel and its constituent quality. Their significance stems from the fact that their presence possesses characteristic importance in the biodiesel produced. However, despite the biodiesel produced deriving its feedstock from waste cooking oil, it possesses a number of characteristics that are distinct from those of its counterpart, crude oil.

Chromatogram at 40 degrees temperature

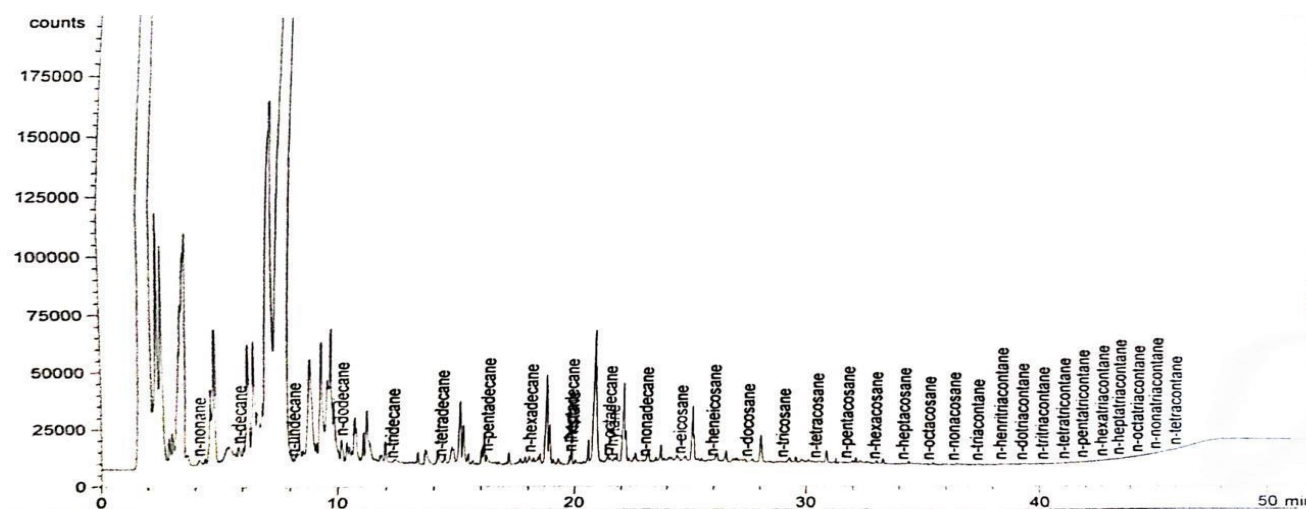


Figure 1: The chromatogram of the biodiesel produced at a temperature of 40 degrees, which contained a total petroleum hydrocarbon content of 1652.65µg/L

Chromatogram at 50 degrees

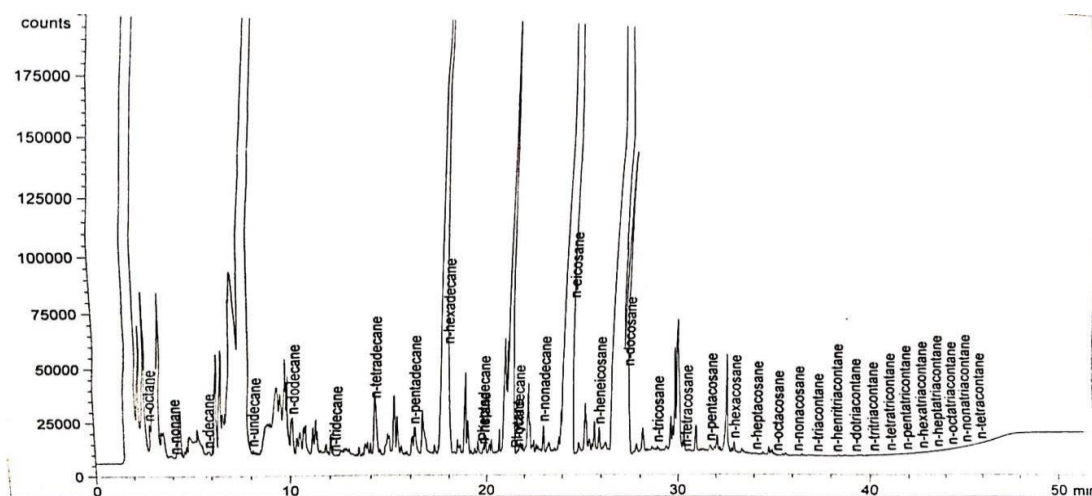
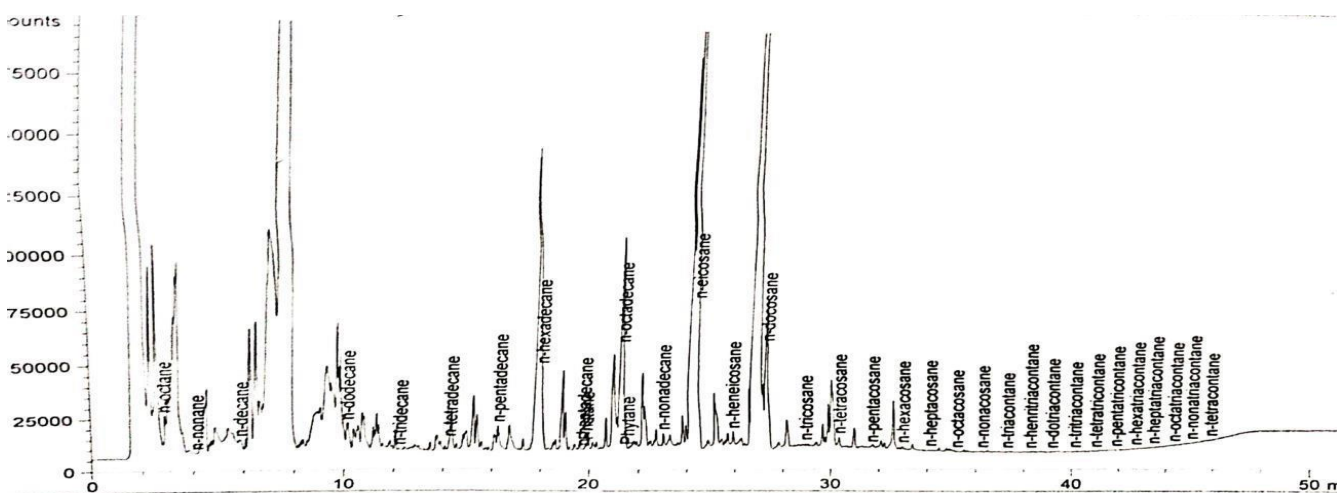


Figure 2: The chromatogram for the biodiesel produced at 50 degrees, which was the temperature that achieved the optimum total petroleum hydrocarbon composition with a content of 9629.803 μ g/L

Chromatogram at 60 degrees



The chromatogram achieved at 60 degrees, containing a total petroleum hydrocarbon of 9608.752 μ g/L

However, from the chromatogram of the biodiesel achieved at varying temperatures the abundance count is seen to be on the vertical axis while time which served as an important function was on the horizontal axis, these parameters aided in obtaining the amount of the total petroleum hydrocarbon present at each temperature phase. Thus, ascertaining the temperature with the highest quality.

Thus, it could be inferred that at 40 degrees the total petroleum hydrocarbon content, TPH was very low which was caused as a result of the insufficient temperature for the transesterification process due to the source of its feedstock, waste cooking oil. And, at 60 degrees the TPH content reduced slightly due to some hydrocarbons evaporating from the system. But, at 50 degrees the biodiesel with the highest quality was obtained having the highest total petroleum hydrocarbon content.

4. Conclusion

This paper addressed Biodiesel, as a potential and sustainable substitute for petro diesel. Thus, it brought about elucidating its several aspects which are stated below:

1. Biodiesel has been proven the best substitute to fossil fuel. It is superior to petroleum based fuels because it is renewable, biodegradable, and non-toxic.
2. The influence of temperature on the total petroleum hydrocarbon was kinetically important, which was carried out at 40, 50 and 60 degrees. The best results were obtained at 50°C. That is, the analysis satisfactorily achieved its aim by obtaining the temperature with the highest total petroleum hydrocarbon content, with the composition of each individual hydrocarbon summing up to obtain the total petroleum hydrocarbon present in the varied temperature.
3. Transesterification is more common in the production of biodiesel than other conversion processes, such as micro-emulsification and pyrolysis.
4. WCO is expected to be more important in the future production of biodiesel than other edible and non-edible oils because of its low cost and wide availability. However, WCO requires several pre-treatment steps to eliminate solid impurities and reduce FFA and water contents. The pre-treatment process may include a washing step, centrifugation, flash evaporation, and acid esterification.
5. Several types of catalysts have been used widely for esterification reaction, such as homogenous catalysts (acidic and basic), heterogeneous catalysts (acidic and basic), and enzymes. Base homogenous catalysts face a large challenge in terms of the FFA and water contents in the oil. Therefore, a two-step process may overcome this challenge.
6. Methanol is used in the transesterification process because of its wide availability, high activity, and low cost. The methanol/oil molar ratio was one of the variables that had more influence on the process. Within the range of molar ratios employed, the best results were obtained for an 8:1 ratio.

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