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Production of biodiesel from orange peels - A senior student project

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Abstract. Biofuel production and utilization are becoming more widespread around the world. One environmentally friendly and economically viable feedstock considered for biofuel production is orange peels (zest). Previous research has documented the viability of using orange oil as an additive for aviation-grade fuel. It has been determined that it is acceptable to mix as much as 15% by volume of treated orange oil with current jet fuels without performance degradation. Prior to mixing with conventional jet fuel, the orange oil must be treated to avoid excessive soot formation during combustion. Hydrogenating the orange oil prior to mixing with jet fuel will diminish this problem. This article reports the results of a ***senior-student project***, in which the processes of orange oil extraction, hydrogenation, and the conversion of orange oil into biodiesel fuel were reviewed. A small amount of biodiesel fuel was produced using orange peels as feedstock. The orange peels collected from several juicer establishments initially had a wet mass of 5130 grams. The peels were dried by the process of sun drying to remove unwanted water. This resulted in a net production of 6.79 ml (5.7 g) of orange oil through steam distillation. We were able to produce 0.03 ml (0.025 grams) of biodiesel fuel in less than 11 weeks. The measured heat of combustion of the biodiesel fuel was 33.65 MJ/kg. The scale of orange peel-based biofuel production must be increased by several orders of magnitude to make this process economically feasible.

Key words. Orange Peels, Biofuel Production, Aviation Fuel, Heat of Combustion

1. Introduction

The global energy consumption continues to rise as the world population grows and more people can bear the expense of vehicles and appliances. The result is a continuous increase in fuel demand, harmful emissions as well as *climate change* as evidenced by recent unprecedented "heat waves" around the world [1],[2].

As the world population continues to depend on more fuel every year, it becomes more paramount to explore renewable, economical, and less damaging alternative fuel sources. Recently, orange peels have been recognized as a feedstock for biofuel production. Oranges are plentiful in many countries around the world. Once extracted from orange peels, the orange oil can be used in the consumer market to manufacture food additives, pharmaceuticals, cosmetics, essential oils, and packaging materials [3]. Orange peels are currently under-utilized, considering that millions of tons of waste are produced annually by orange juice manufacturers.

One such usage of orange peels is their conversion into biofuel due to the high amounts of D-Limonene found within the peel, and the excellent density and calorific value [4]. Many studies done on D-Limonene prove that this chemical has excellent intrinsic properties for biofuel conversion [5], [6]. Production of biofuels is a critical scientific development because instead of relying on non-renewable resources to power the society's various methods of transport (cars, planes, trains, etc.), biofuels are produced from renewable resources, such as orange peels and algae [7]. As biofuel research continues to develop, new applications of biofuels are discovered incessantly [8].

A prominent application of biofuels is their usage as jet fuel. The density and calorific value of D-Limonene are comparable to those of jet fuel [9]. A study done at the University of Central Florida investigated the use of orange peels to produce orange oil and turn the oil into ethanol and jet fuel while supplying new jobs to 1200 of Central Floridians [10].

Extensive research has been done on D-Limonene extraction and purification. Usage of steam distillation and solvent extraction have shown to produce the needed chemical [11]. Once this chemical has been extracted, it must be combined with other reactants to turn it into a biofuel. This process usually occurs through a transesterification reaction, and the catalyst used in this process tends to vary. One study chose biomass-derived sulfonated orange peel as the catalyst [12]. Another study chose sodium hydroxide as their catalyst and provided details on the extraction and separation process of D-Limonene [13].

2. Orange Peel Collection and Oil Separation

To begin the biodiesel production process, initial calculations were performed to determine the amount of orange peels needed to produce the wanted yield of 20 ml of biodiesel. From a rough approximation, it was determined that 8 full-sized oranges produce roughly 117 g of orange peels, or 14.6 g per orange. To determine the amount of oranges needed, a process of extracting the orange oil had to be chosen. Four processes were considered, steam distillation, water distillation, solvent extraction, and cold pressing. Their respective reported yields are 4.40%, 3.47%, 2.54%, and less than 1% [14]. While cold pressing would be the easiest method to extract the orange oil, steam distillation was chosen due to its higher yield per orange peel mass [15]. It was determined that a minimum of 34 oranges will be needed to produce the desired 20 ml of biodiesel by factoring in orange oil's density of 0.84 g/ml [16]. Following generous donations from local Flint and Davison juicer establishments, 5.13 kg of orange peels were collected as seen in Fig 1.

Fig. 1 Collected orange peels

Following the collection of orange peels, all excess flesh was removed. In order to dehydrate the orange peels to yield more orange oil [17], the peels were placed in air-tight containers and allowed to sun-dry for two days, resulting in the condition shown in Fig. 2. Oven-drying was used at first, but it over-dried the orange peels causing them to wrinkle and possibly lose the wanted orange oil. Once the dehydration process was complete, the dried orange peels were ground up using a blender and stored in an air tight container until laboratory usage, as seen in Fig. 3.

Fig. 2 Dried orange peels

Fig. 3 Ground orange peels measured for steam distillation

The first step of the oil separation process utilizes the chosen method of steam distillation to extract orange oil from an aqueous solution of ground orange peels and deionized water [18]. Two batches of distillation occurred, each with an approximate 2:1 ratio of ground orange peels and deionized water. Approximately 150 g of orange peels were used between the two batches. The solution was placed in a 500 ml round-bottom flask and placed onto a heating device, which heated the solution at a gaseous air temperature of 100 °C for two hours. A tube was attached to the round-bottom flask which contained an outer layer of cold water, with the inner layer emptying into a small beaker into which an oil and water mixture was collected. See Fig. 4 for images of the steam distillation setup. Approximately 350 ml of oil and water solution was collected during steam distillation.

Fig. 4 Steam distillation setup. A 500 ml round-bottom flask contained the solution, while a thermometer and tube were attached to the top for distillation to occur and be monitored.

To separate the orange oil from the water, hexane washing was utilized. A 500 ml separatory funnel was used to hold a mixture of the oil and water solution in addition to approximately 100 ml of hexanes. Due to the oil's molecular attraction to hexane compared to water, a clear separation was seen in the separatory funnel after washing and mixing occurred (Fig. 5). The mixing process involved shaking the oil/water mixture with the hexanes until pressure was not released while opening the pressure valve. Six washing cycles were used for each of the two steam distillation batches. Approximately 900 ml of an oil and hexanes mixture was obtained following this process.

Fig. 5 Five hundred ml separatory funnel containing hexanes mixed with orange oil (top layer) and water mixed with oil (bottom layer)

To separate the orange oil from the hexanes, the Rotavapor device shown in Fig. 6 was utilized. Small amounts (≈ 100 g) of the oil and hexanes were added to a round-bottom flask to be placed onto a Rotavapor. The Rotavapor evaporates the hexanes from the solution in the flask and dispenses it into a collection flask. What remains in the round-bottom flash is pure orange oil. Following 7 cycles of evaporation, 5.7 g of pure orange oil was collected from the initial 150 g of ground orange peels. This resulted in a 3.8 % yield, slightly less than the 4.4% yield reported in the literature [14].

Fig. 6 Rotavapor setup

3. Biodiesel Production

A transesterification reaction was used to convert the 5.7 g of pure orange oil into biodiesel [19]. For this reaction to occur, an alcohol and catalyst must be present to convert the D-Limonene found in orange oil into usable biodiesel. First 15 ml of methanol was heated to 55-60 °C and then combined with the orange oil. Potassium hydroxide (93 mg) was then added to this solution and placed over a hot plate, which maintained the temperature at 55-60 °C. A stir bar was placed into the 25 ml flask containing this alkaline solution, and a reflux condenser was placed over the flask to condense any evaporated oil back into the reaction. This continued for two hours and then the contents were transferred to a small separatory funnel to allow the glycerol and biodiesel to separate following the initial cooling (Fig. 7).

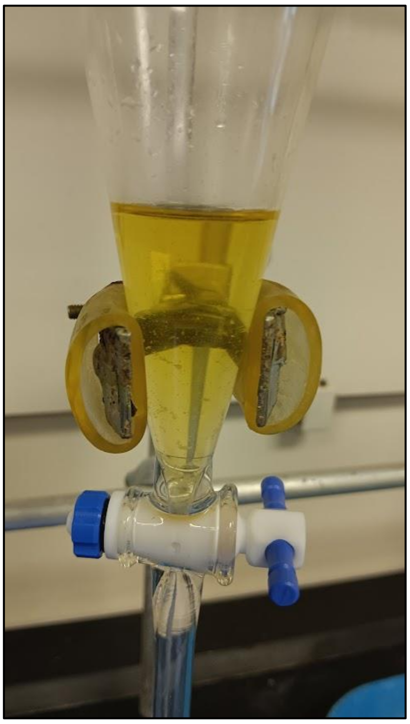

Fig. 7 The transesterification reaction

As seen in Fig. 7, there is no clear layer of glycerol and biodiesel. During a discussion with the Chemistry Department staff, it was determined that traces of water was mixed in with the reaction, causing the catalyst to be ineffective and a "soapy" solution to form. To remedy this issue, it was decided that adding molecular sieves to dehydrate the solution would be a viable option. This was followed by additional hexane washing and evaporation to further separate the biodiesel from the "soapy" solution. Seen in Fig. 8 is the container of the molecular sieves used. Following these repeated processes a final yield of 25 mg of biodiesel was obtained as seen in Fig. 9.

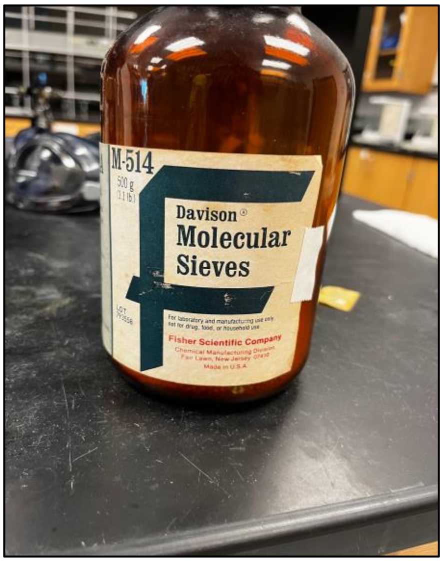

Fig. 8 Molecular sieves for dehydration of the "soapy" biodiesel

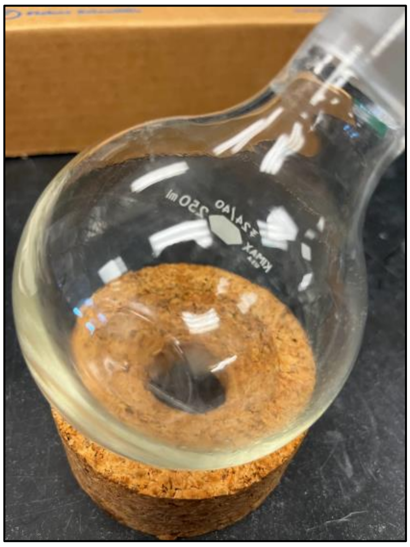

Fig. 9 Twenty five mg of pure biodiesel

4. The Results

The production of biofuel from approximately 150 grams of dried orange peels revealed some interesting findings. It's important to note that not all the dried orange peels were utilized in the project. Additionally, alternative methods for orange oil production were considered but not employed. The approximate yield of the biofuel obtained from the orange peels was around 0.025 grams, representing an overall biofuel yield of approximately 0.02%. Unfortunately, there was insufficient biodiesel from the orange peels to conduct a separate calorimeter test.

To understand the properties of the obtained biofuel, we ran one pure hexanes sample and three samples where hexanes were mixed with the biodiesel. In terms of temperature change (ΔT), the average for samples 1-3 was approximately 3.01 Kelvin, while the specific heat capacity (C) averaged around 8.368 kJ/kg*K. The total heat transfer (Q) for these samples averaged approximately 25.188 kJ, with a lower heating value (LHV) of about 33.65 MJ/kg and a higher heating value (HHV) of approximately 37.35 MJ/kg.

When it comes to the pure hexane, the temperature change was $\Delta T \approx 3.09$ K, slightly higher than the mixture samples. The specific heat came out to be $C \approx 2.26$ kJ/kg*K, resulting in a heat transfer of 6.983 kJ. The calculated LHV was 38.97 MJ/kg and HHV of 43.26 MJ/kg.

These results highlight the differences in thermal properties between the obtained biofuel from orange peels and pure hexane. While the biofuel showed a lower LHV and HHV compared to hexane, it exhibited a higher specific heat capacity, suggesting potential for further optimization and exploration in biofuel production from orange peels. If a pure sample of biofuel was obtained, a calorimeter test would be able to better distinguish variability.

It is important to acknowledge any discrepancies within our gathered data. Typically, when determining heat transfer

(Q), the formula $Q = C_{cal} * \Delta T$ is used, C_{cal} denotes the specific heat of the calorimeter. Unfortunately, this value was not known for the equipment used. Instead, our calculations relied on data values for C and ΔH_{vap}, obtained from external references [20]-[23].

5. The Cost

Thanks to assistance from the Kettering University Chemical Engineering Department and donations by local juicers in Flint, Michigan, the project had a minimal cost of only $15 from the allotted $300 budget. The $15 was spent on the initial collection of oranges prior to finding free sources and cheesecloth for drying out the oranges.

6. Safety Considerations

Converting an oil to biodiesel fuel is often accomplished by using methanol, also known as methyl alcohol (or alternatively isopropyl alcohol), and lye (sodium hydroxide, NaOH).

The oil is first heated to 54-60 °C (130-140 °F). Next, the methanol and lye are mixed to form a methoxide solution. Caution must be exercised during this step, as this mixing is an exothermic process. If the compounds are mixed too quickly, and the boiling point of methanol, 64 °C (148 °F), is exceeded, a violent explosion can occur.

Once the lye is dissolved in methanol, the methoxide solution can be added to the heated oil while stirring continuously. This combination causes transesterification - a process by which "the oil and methanol crosscut one another's chemical bonds to form new chemical bonds." When this is complete, two compounds result: biodiesel and glycerol.

The solution is then left to settle for a period of about 24 hours, during which the biodiesel and glycerol separate owing to their different densities. One or the other can then be removed from the container.

Before use in a combustion engine, the biodiesel must be washed and filtered until its concentration reaches B100 (100% biodiesel). This is roughly the same process that would be used in a large-scale biodiesel operation. The only difference is that specialized equipment would be used to efficiently heat, mix, and separate the various compounds in much larger quantities.

Methanol is a volatile and flammable liquid with a distinctive alcoholic scent. Ingesting as little as 10 ml of pure methanol can cause permanent blindness by destruction of the optic nerve. Thirty ml is potentially fatal.

Lye is a caustic substance. It can burn or corrode organic tissue. It can damage exposed skin and cause burns, blindness, and even death when consumed.

For these reasons, the process of transesterification should only be carried out with extreme caution while wearing an approved lab coat, goggles, and gloves.

7. Conclusions and Lessons Learned

During the execution of this project, there were some lessons learned that should be taken note of. It would be beneficial to perform the lab procedures in incremental steps throughout the school term rather than attempting to rush the procedures. This could be accomplished by collecting sufficient sample material (orange peels) earlier in the term to provide as much time as possible for the lab work. In addition, it would help to upscale the processes in some way to increase the product yield. With the small-scale equipment and sample sizes used, only a small yield was attainable after hours of lab work. Also, extra caution must be exercised when conducting lab experiments as the smallest accident can lead to scrapping trials and hours of work when a sample becomes contaminated or measured incorrectly.

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