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DEVELOPMENT OF A CARBON CATALYZED PROCESS FOR THE  
PRODUCTION OF BIODIESEL FUELS

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## ABSTRACT

This investigation aims to investigate the possibility of improving the process of synthesizing biodiesel fuels by the addition of activated charcoal to simplify the product purification processes. With the purification steps comprising a significant amount of biodiesel production time and cost, such a process improvement would have tremendous benefits.

Activated charcoal was first identified as a viable additive that could both absorb water and adsorb solids to its surface. Charcoal was selected as the agent of investigation based on its potential shown in previous research and testing. Various deviations to the standard biodiesel production process by which activated charcoal was added to the reaction mixture were investigated. The resulting products were qualitatively assessed by FTIR, water content, kinematic viscosity, and product percent yield. The results were compared with a biodiesel sample produced by the standard methods to determine the benefits, if any, of using the activated charcoal medium throughout the synthesis process.

Using charcoal as an agent to purify synthesized biodiesel was found to be effective, while using charcoal as a component in the reaction mixture was ineffective in improving biodiesel composition. The addition of this solid was found to have negative effects on the product yield and water content of the product when it was added to the mixture during the reaction. However, charcoal was deemed a viable alternative to the standard water wash and water removal purification steps when the charcoal is added to the synthesized biodiesel product. Such uses of charcoal in biodiesel production are recommended for further analysis and cost evaluation, as this study has proven them to be legitimate alternatives.

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## **Chapter 1**

### **Introduction**

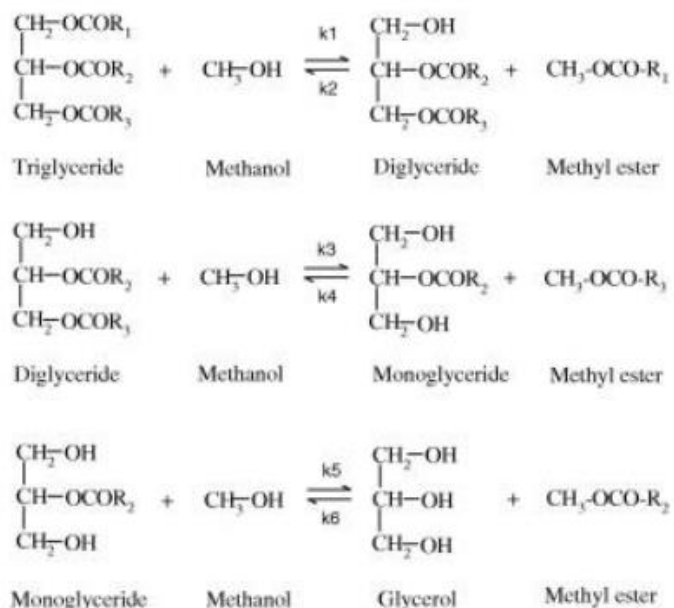
Global energy demands continue to increase day by day, so it is extremely important that alternate energy sources are being explored as we look to a more sustainable future. Today, 86% of the energy being used around the world and nearly 100% of the energy used in the transportation sector is being provided by non-renewable fossil fuel sources (1). This is concerning because fossil fuels are being depleted at a rate much more significant than the rate that they are being regenerated. Additionally, the burning of fossil fuels is harmful to the environment, and is thought to cause environmental pollution and global warming due to greenhouse gas emissions (1). The continued use of fossil fuels as our major (and essentially our only) energy source is not sustainable for a growing global population, growing environmental concerns, and growing energy demands. Therefore, it is important that alternative sources of energy are investigated.

Biodiesel fuel is considered to be a “renewable, biodegradable alternative to petroleum diesel,” and is “one of the most promising diesel fuel substitutes” (2). Biodiesel is one of the best alternatives in terms of the environment—one that is carbon neutral, since the plants which produce the reactants for biodiesel production consume more carbon-dioxide than is produced by the combustion of biodiesel (1). Many countries, especially in the European Union (EU), have recognized the potential of biodiesel as a large scale energy source. In fact, the EU has set a goal to have 20% of its motor fuel consumption to be comprised of biodiesel fuels by 2020 (3). Thus, various procedures for producing biodiesel fuels are being investigated, and are subject to

analysis and improvement to make them the most efficient processes possible. With the ultimate goal of global biodiesel fuel usage, efficient synthesis processes are required.

### Trans-esterification Reaction

The most common mechanism for biodiesel synthesis is through an alkali-catalyzed transesterification reaction of a vegetable oil with methanol, which leads to a fairly short reaction time (4). Overall, the transesterification reaction consists of three elementary reactions, each of which cleaves one of the three fatty acid chains from the starting oil, known as the triglyceride or triacylglycerol. The result is three fatty acid esters (the biodiesel product), and one glycerol molecule. The schematic in Figure 1 summarizes the series of three elementary reactions which comprise the overall transesterification reaction of a triglyceride to biodiesel fuel.



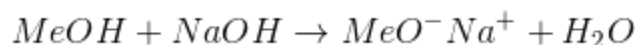
**Figure 1: Elementary reaction schematic for biodiesel formation by transesterification (5)**



In this reaction mechanism, each of the elementary steps is reversible, so the overall reaction can never reach 100% completion. Each elementary step is governed by rates of reaction, with the second elementary step (diglyceride to monoglyceride) being slower than the third elementary step (monoglyceride to glycerol) (5). As a result, there are unconverted starting materials, or partially converted materials (diglycerides and monoglycerides) present in the reaction mixture.

It is then desired to push this reaction far towards the desired biodiesel products and avoid partially or non-converted glycerides. Excess methanol is typically used in reaction in order to drive the reactions forward towards producing the biodiesel products, increasing desired product yield and assisting with phase separation from the glycerol (6). By using methanol in extreme excess, this ensures that there is always methanol available to react with the glycerides, allowing each elementary step's equilibrium to be weighted heavily towards the product side.

The use of a homogenous alkali catalyst, like NaOH is commonly employed to increase reaction yield of biodiesel. The homogeneous catalyst will be evenly mixed through the reaction mixture, allowing for a rapid reaction since the reactants and catalyst are easily brought in contact by vigorous stirring. One study found that a sample of triglycerides were completely transesterified (~100% yield) after only 5 minutes of reaction at room temperature (298K) in the presence of a homogeneous catalyst (6). By mixing the catalyst with methanol to form a pre-reaction broth prior to adding it to the reaction mixture, this will produce a sodium methylate in water solution as seen in Figure 2.



**Figure 2: Sodium Methylate Formation Reaction**

In the reaction shown in Figure 2, the products are heavily favored. Therefore, the pre-reaction broth will be composed mainly of sodium methylate (MeONa) and water produced by the reaction mixture. When added to the base oil (for this series of experiments, Canola oil was

used as the base oil in all runs for a basis of comparison) the sodium methylate easily dissociates into its two ions:  $\text{MeO}^-$  and  $\text{Na}^+$ . The methylate ion will then be readily available in solution to react with the glycerides to form biodiesel, following the reaction mechanism in Figure 1. Thus, it is clear that the use of the NaOH homogeneous catalyst will facilitate a further biodiesel yield by producing methylate ions to react with the base oil.

### **Opportunities for Improvement**

The post reaction mixture will contain a large fraction of desired biodiesel product, but will also contain the glycerol product, water, and other reaction byproducts. These contaminants must all be removed to provide a purified biodiesel product that is usable on a wide scale. The feedstock accounts for about 70-80% of the process expense, with the purification steps accounting for 20-30% of total process expenses. Since feedstock costs depend on supply and demand and are relatively uncontrollable, it is clear that biodiesel product purification is the more viable area for investigation, improvement, and resulting cost savings.

The glycerol product is separated from the biodiesel product by a difference in density. The glycerol ( $\rho = 1.26 \text{ g/mL}$ ) and biodiesel ( $\rho_{\text{avg}} = 0.88 \text{ g/mL}$ ) have significantly different densities, and can thus be easily separated from one another. There is little that can be done to avoid this purification step, given that glycerol and biodiesel will be the primary reaction products. In major production facilities, centrifugation is used to accelerate this separation step.

In the general process, a water wash is then used to remove catalyst residues and remaining glycerides. This water is also removed by settling or centrifuging, but is not completely removed. Removing the water from the product is time consuming and expensive. Current techniques include using a drying agent (like magnesol) post-glycerol separation, but this can be

expensive to purchase the agent, and time consuming to combine and then filter this mixture. Another option is to gently heat the biodiesel product in an attempt to evaporate any water that it may contain. This is also very time consuming, and can be difficult to use effectively since the amount of heating needed will depend on how much water is in the sample to start, but this value is subject to change from sample to sample. Distillation is another option, but is again very costly and time consuming.

Overall, it was clear that an opportunity is available to improve upon the purification steps of the biodiesel fuel product. In this study, a variety of process deviations using activated charcoal additive were explored as potential methods to eliminate purification steps including both the water wash and water removal, while maintaining the required biodiesel product purity.

## **Chapter 2**

### **Experimental**

#### **Materials Used**

1. Canola oil (WEIS, Sunbury, PA, USA) and Canola oil (Great Value, Bentonville, AZ, USA) were both purchased at a local food store
2. Methanol (99.8% purity, EMD Chemicals, Darmstadt, Germany)
3. Sodium hydroxide (pure NaOH, Duda Diesel LLC, Madison, AL, USA)
4. Activated charcoal (Granular Activated Charcoal, [www.buyactivatedcharcoal.com](http://www.buyactivatedcharcoal.com))
5. Solvents and analytical reagents were of standard grade.

#### **Equipment Used**

1. FTIR was used to check product quality by checking for water and methanol content in the biodiesel. The FTIR analysis was performed using an i-S-10 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA)
2. Karl Fischer Titration was used to measure water content using a Coluometric Karl Fischer Titration Module (Denver Instrument Company, Arvada, CO, USA)
3. Kinematic viscosity data was collected using an automated kinematic viscometer (Cannon Instrument Company, State College, PA, USA).

## **Chapter 3**

### **Procedure**

The standardized lab procedure for synthesizing biodiesel was used as a base case for all investigative work. The scale of each experiment was downsized slightly from the standard procedures, such that only moderate quantities of each sample were produced. The first runs produced standard biodiesel samples. Subsequent samples introduced activated charcoal in various quantities at select points in the synthesis or purification processes. The objective was to assess the effect of the activated charcoal on the need for additional water wash and water removal steps. Therefore, neither a water wash step nor any additional water removal steps (magnesol, heating, or otherwise) were utilized in these trial runs. The “unprocessed products”, collected after the density-based glycerol separation step, were assessed for each case. Quality control tests were performed in order to assess both the quantity and composition of biodiesel product produced through each variation explored.

#### **Standard Procedure**

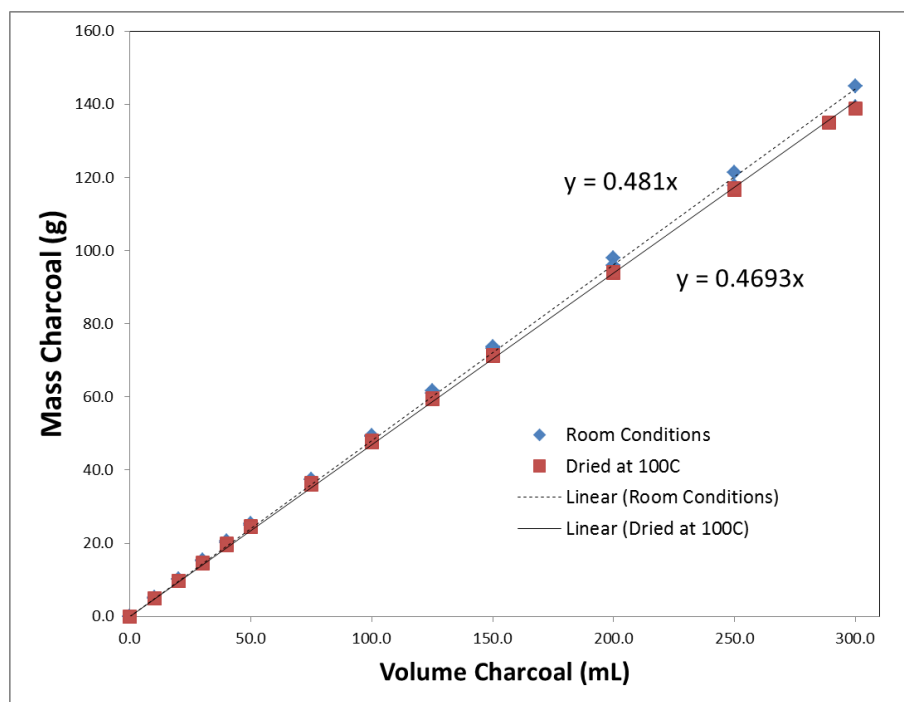
100.0 mL of canola (rapeseed) oil was heated to a reaction temperature of 55°C. In a separate vessel, 20 mL of methanol and approximately 0.350 g of sodium hydroxide were stirred for 15 minutes to make the pre-reaction broth. The pre-reaction broth was added to the heated oil, which continued to be stirred and maintained at reaction temperature as the reaction proceeded for 45 minutes. After the reaction, the reaction mixture was poured into a separatory funnel and allowed to sit for at least one hour. The lower, denser glycerol layer was removed and discarded. The upper layer was collected as the biodiesel product (7). Note that no additional water wash or water removal steps (aside from the various additions of activated charcoal) were conducted for

any runs. This allowed for direct comparison of the unprocessed product composition between runs, and the effect of the activated charcoal in appropriate runs.

### **Selection of Activated Charcoal Medium**

In general, there are two main areas of investigation: can we use a substance to remove water that is present in the product mixture, or can we use a substance to avoid the introduction of water to the reaction mixture in the first place (recalling that the sodium methylate mixture is aqueous upon addition to the reaction mixture). Therefore, the desired additive should be able to absorb water, and also to adsorb other solids to its surface. Activated charcoal is a low-cost substance that has extremely high adsorption abilities. One teaspoon of charcoal has a surface area of more than 10,000 square feet, and it acts like a sponge to adsorb molecules (8). Therefore, it was believed that charcoal would be an effective resource to use for this investigation.

First, it must be confirmed that the charcoal itself has the ability to hold a small amount of water. Since there is only minimal water in the biodiesel fuel anyway, just a small capacity to hold water is needed from the charcoal. To confirm this, the plot in Figure 3 was created to observe mass versus volume for a sample of the charcoal at room temperature as compared to a charcoal sample that had been dried overnight at 100°C to evaporate all water it may have absorbed from the air in the room. The slope of the best fit line for each case will represent the density of the charcoal (mass/volume).

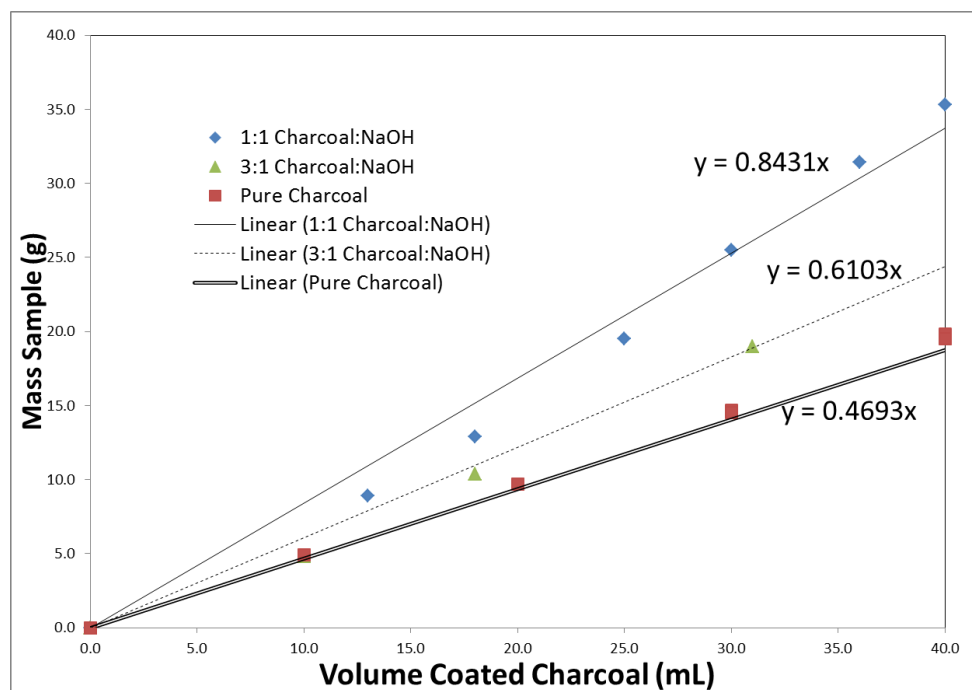


**Figure 3: Mass vs. Volume of Charcoal**

Figure 3 shows the room condition sample to have a density of 0.481 g/mL while the dried sample (and thus the charcoal) was found to have a density of 0.469 g/mL. The difference in density is due to water that was absorbed by the room condition charcoal. By a simple difference, it is seen that approximately 0.012 g water / mL charcoal was absorbed. Through a density calculation, this then means that 0.026 mL water can be held per gram of charcoal at room temperature. This capacity will be sufficient for the experiments at hand, given that only small quantities of water will be present in the reaction mixtures to be absorbed by the charcoal.

Next, it must be confirmed that the charcoal has the ability to adsorb solid onto its surface. This will allow adsorbed reactants to be introduced to the reaction mixture in the absence of water. To test this statement, various charcoal to sodium hydroxide mass ratio mixtures were observed. In each mixture, the NaOH was dissolved thoroughly in 100.0 mL of distilled water and then combined with dry charcoal. The mixture was then put in the heating chamber overnight

to fully evaporate all water. Figure 4 plots the mass vs. volume data for each ratio, allowing the density of each to be determined by the slope.



**Figure 4: Mass vs. Volume Coated Charcoal**

The 3:1 Charcoal:NaOH mixture (minimal NaOH relative to charcoal) resulted in a mixture of dry density 0.610 g/mL. This compared to the pure charcoal density of 0.469 g/mL shows that 0.141 g of NaOH was adsorbed per mL of pure charcoal. Subsequently, the 1:1 mass mixture (equal masses of charcoal and NaOH) gave a dry mixture with density 0.843 g/mL, which means that 0.374 g of NaOH was adsorbed per mL. It is seen that the 1:1 ratio mixture adsorbed approximately three times as much NaOH onto the charcoal as did the 3:1 mixture (0.374 g/mL vs. 0.141 g/mL), which correlates directly with the 1:1 mixture having three times as much NaOH present in the mixture as the 3:1 ratio mixture. It is then concluded that activated charcoal is able to adsorb solid onto its surface, and that it can do so at a capacity directly proportional to the amount of solid NaOH originally in the mixture. Thus, activated charcoal was deemed a viable option to use for this study.



### Charcoal Deviations

Since charcoal was deemed a viable agent to both absorb water and also to introduce adsorbed reactants, a series of variations on the standard biodiesel synthesis procedure were conducted. In the first deviation, varying amounts of dry charcoal were introduced into the reaction mixture just prior to the 45 minute reaction period. The charcoal was removed in the filtration procedure after the reaction was complete.

The second deviation introduces dry charcoal later in the process. Biodiesel samples were synthesized and separated from the glycerol layer via the standard procedure. Then, the final biodiesel samples were mixed with charcoal to attempt to remove any additional impurities present. The charcoal was then removed from the sample via a second filtration process.

The third deviation uses charcoal to introduce the sodium hydroxide to the pre-reaction broth. Specified amounts of NaOH were dissolved in water, and then mixed with charcoal and dried overnight to adsorb the NaOH on the charcoal. The coated charcoal was then mixed with the methanol to make the pre-reaction broth, which was then introduced to the heated canola oil for the reaction to occur. The charcoal was removed via filtration after the reaction.

The fourth and final deviation adsorbed the sodium methylate on the charcoal. The pre-reaction broth was created, and then mixed with dry charcoal. The mixture was put in the heating chamber overnight. Recalling that the pre-reaction broth was composed mainly of aqueous sodium methylate, this deviation seeks to introduce the sodium methylate to the reaction mixture without the addition of water or excess methanol. The charcoal with sodium methylate was directly added to the heated oil for the reaction to occur. The charcoal was removed in the filtration procedure.

Overall, these four deviations serve to investigate the effect of introducing charcoal to the reaction at various points, and the possibility of adsorbing reactants to the charcoal to introduce them to the reaction mixture.

### **Viscosity Test**

The viscosity of each sample was measured using the automated kinematic viscometer apparatus. The sampling cup was filled approximate two thirds full with the sample to be tested (about 10-15 mL) and placed in the sample cradle. The testing apparatus tip was put into the sampling cup, and a series of drop tests were automatically conducted to measure the average kinematic viscosity. The viscosity values for each sample were displayed to a screen in units of centistokes (cSt). The unit employs an auto cleaning mechanism by which heptane solvent cleans the apparatus between runs. The ASTM standard for kinematic viscosity of biodiesel fuel is between 1.9 and 6.0 cSt (7). The viscosity of the canola oil feedstock was measured to be 36.0-37.0 cSt.

### **IR (Infrared Spectroscopy) Test**

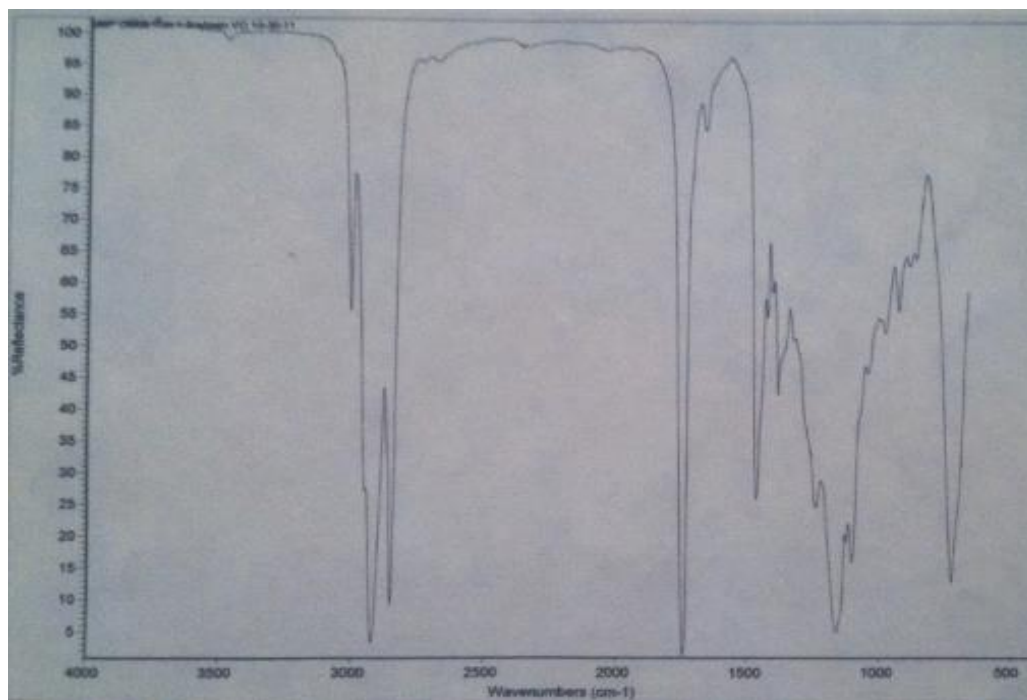
A FTIR spectra for each sample was generated using the FTIR spectrometer. A pipette was used to load a sample into the testing window, such that the window was completely covered by the sample. The cover was closed, and the program generated the desired spectra for each sample. IR spectroscopy passes a beam of light through the sample and measures what frequencies of light are absorbed by the sample. The spectra show peaks at given wave numbers based on these absorptive properties, which allow functional groups in the sample to be

identified. Table 1 summarizes key functional groups and their associated wave numbers that may be observed on IR spectra.

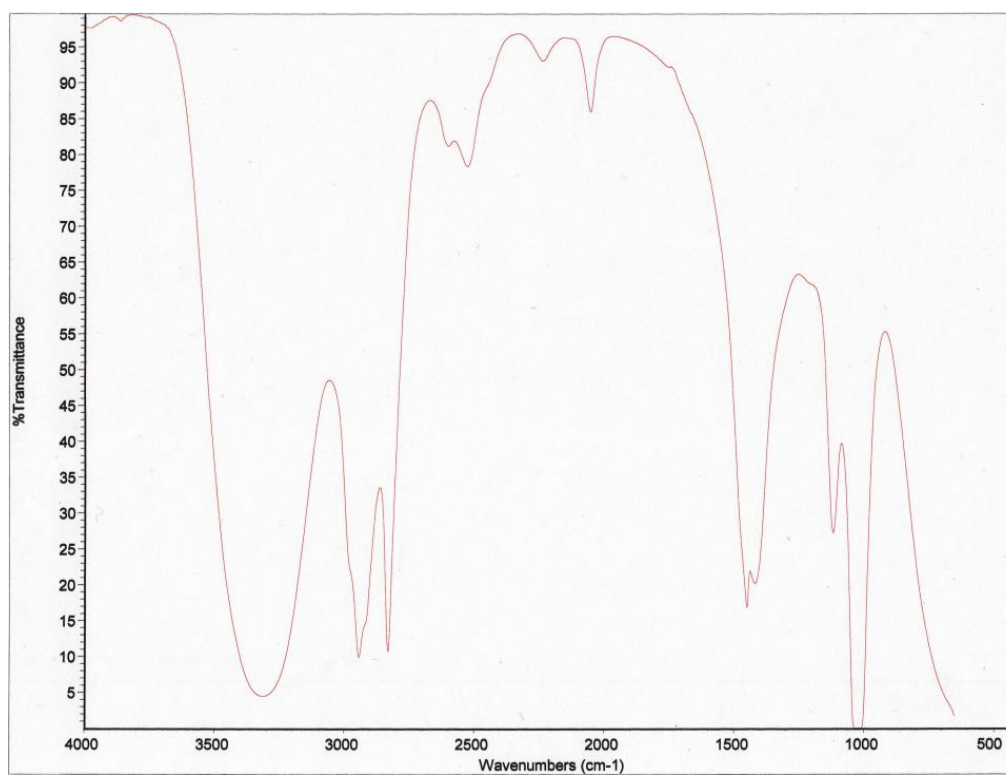
**Table 1: Wavenumbers observed on IR spectra for certain functional groups (7)**

Functional group	Waverange number
O-H	3300-3500
C=C-H	3000
CH <sub>3</sub>	2900
CH <sub>2</sub>	2800
C=O	1745
C=C	1400
COO (ester)	1150-1200
(-CH <sub>2</sub> -) <sub>4</sub>	740

As a basis for comparison, IR spectra for samples of known biodiesel and known methanol were collected. Figure 5 is the standard biodiesel spectra, and Figure 6 is the standard methanol spectra. By observing these spectra, a standard basis for observable absorption peaks can be created to allow for comparison and evaluation of the IR spectra for each of the experimental biodiesel samples.



**Figure 5: Biodiesel Stock IR Spectra**



**Figure 6: Methanol Standard IR Spectra**

In analyzing Figure 5, the standard absorption peaks for a stock biodiesel sample can be observed. The strong peak around  $1750\text{cm}^{-1}$  indicates the presence of the ester making up the biodiesel fuel. The peaks around  $2800\text{-}2900\text{cm}^{-1}$  represent the hydrocarbon chains present in the biodiesel. This spectra represents the standard absorption peaks and general format that will be observed for a biodiesel fuel sample. In the methanol spectra in Figure 6, the noticeable absorption peak around  $3400\text{cm}^{-1}$  represents the presence of an  $\text{-OH}$  functional group. Whenever this peak is observed on a biodiesel sample spectra, this indicates that the  $\text{-OH}$  function group is present, signifying that methanol or water is contaminating the biodiesel sample. The stronger this specific absorption peak, the higher the methanol and water content of the sample. Therefore, as biodiesel samples are investigated, a minimal or nonexistent absorption peak in this position is desired.

### **Water Content Test**

Karl Fischer titration was used to determine the water content of each sample. A sample of known mass was injected into the Coulometric Karl Fischer Titration Module, which uses an acid base titration system to determine the amount of water contained in the sample, giving the result in units of parts per million (ppm). The ASTM standard for acceptable water content levels in biodiesel fuels is below 500 ppm (7).

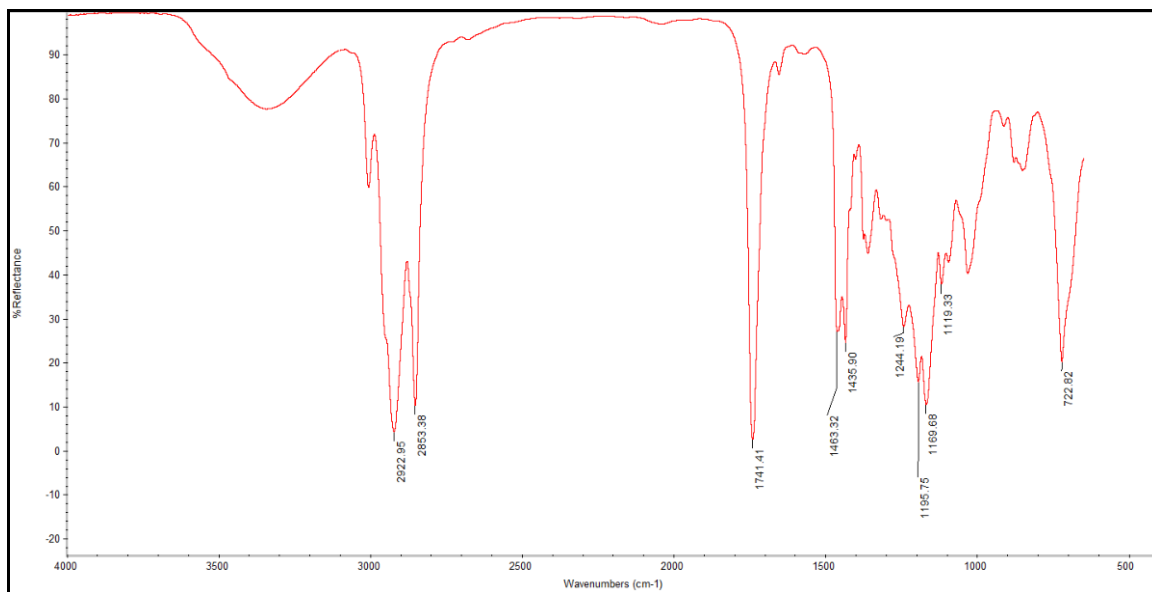
## **Chapter 4**

### **Results and Discussion**

To evaluate the success of each potential charcoal introduction technique, a biodiesel standard was synthesized. Various biodiesel samples were then synthesized by each charcoal deviation technique. Each sample was characterized by viscosity, IR, and water content testing, as well as percent yield calculations. The sections below evaluate the results and effectiveness of each potential technique to determine which, if any, are recommended for further use.

#### **Standard Tests**

Two runs of biodiesel were synthesized using the standard procedure to establish a baseline for comparison of the various process deviations employing activated charcoal. The data between the two trials was averaged to develop a single standard. An average 94.73% yield based on the initial mass of canola oil was observed, suggesting that the standard procedure is very efficient with little loss of mass. An average water content of 115 ppm was observed, which meets the ASTM water content standard, without the need for any additional water purification steps. The average kinematic viscosity was found to be 5.80 cSt for the standard samples, which falls within the ASTM range for biodiesel fuels. Figure 7 shows a representative IR spectra for the biodiesel fuel standard.



**Figure 7: Biodiesel Experimental Standard Representative IR Spectra**

All peaks in this figure, other than the  $3400\text{cm}^{-1}$  peak, represent the standard absorption peaks seen for biodiesel fuels. This confirms the identity of the sample as biodiesel. Focusing on the absorption peak at  $3400\text{cm}^{-1}$ , it is clear that some water and an unacceptable amount of methanol remained in the sample. Overall, it is clear that the standard biodiesel synthesis procedure produces fairly high quality biodiesel without any additional water wash or purification steps. Both the water content and viscosity values fall within the ASTM established ranges, and the percent yield is relatively high. However, there are still impurities present, specifically methanol, which must be removed. Therefore, each potential charcoal deviation will be evaluated to determine if the water and methanol content of the sample, and the viscosity of the sample can be maintained or improved, while also increasing the percent yield of the biodiesel fuel.

### **Deviation 1: Addition of Charcoal to Reaction Mixture**

In this deviation, various mass charcoal amounts were added directly to the reaction mixture just prior to the 45 minute reaction time. The charcoal was filtered out as the reaction

mixture was transferred to the separatory funnel. Table 2 summarizes the quality tests conducted on each of the samples synthesized by this method deviation.

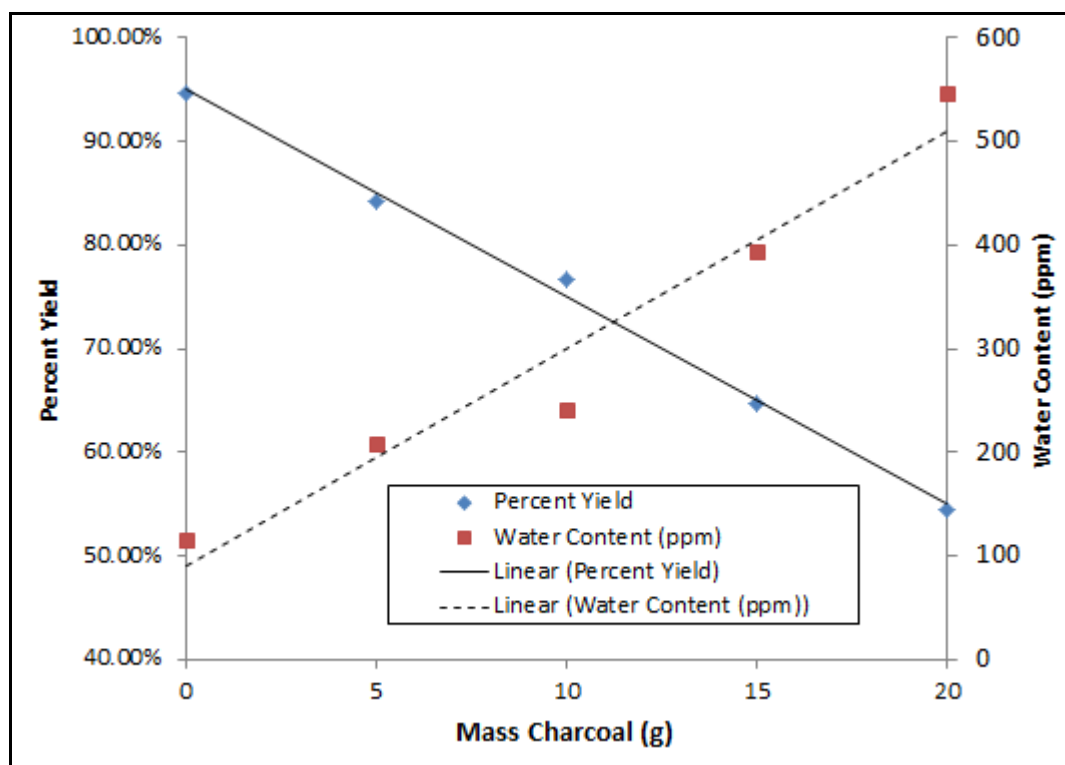
**Table 2: Deviation 1 Quality Testing Results**

Mass Charcoal (g)	Percent Yield (from 100mL oil)	Water Content (ppm)	Kinematic Viscosity (cSt)
0.0	94.73%	115	5.80
5.0	84.26%	209	6.02
10.0	76.60%	240	5.89
15.0	64.64%	394	6.01
20.0	54.53%	546	6.99

First, it must be confirmed that each sample produced is biodiesel fuel. The easiest way to confirm this is to consider the kinematic viscosities of each sample. The average kinematic viscosities in Table 2 show that each sample falls either in the ASTM standard range of 1.9-6.0 cSt, or just above the upper limit. Therefore, it can be concluded that each of the samples was in fact converted to biodiesel fuel during the reaction, and that there are only limited glycerol, diglyceride, and triglyceride molecules present in the final product based on the fact that the measure kinematic viscosities fall within the ASTM standard range.

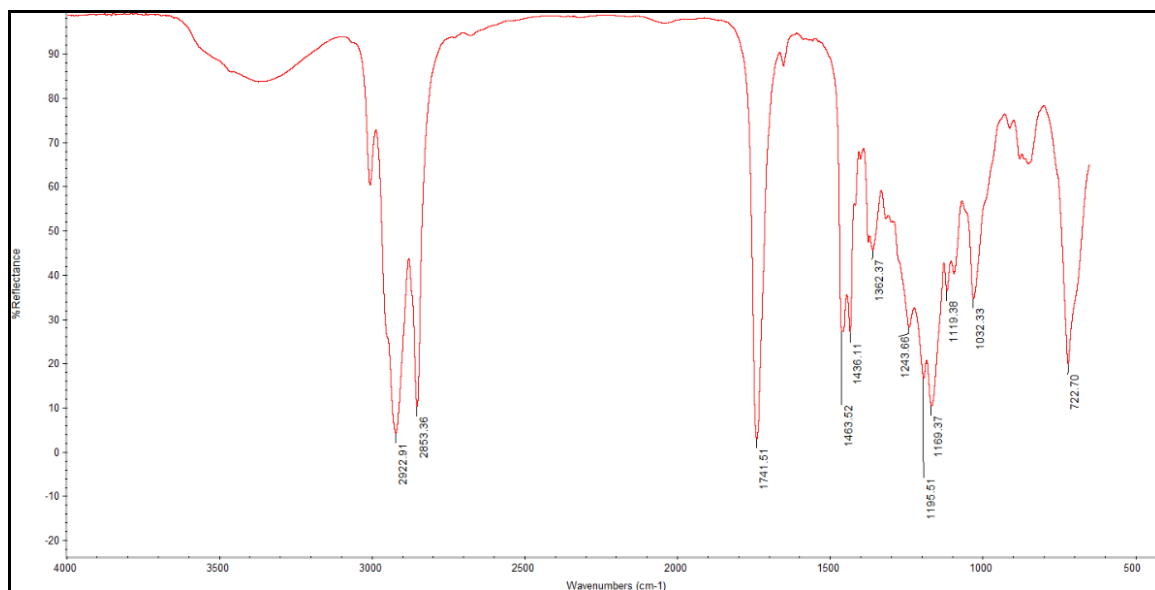
Next, average percent yield is considered for each run. The plot of average yield vs. mass of charcoal used is seen in Figure 8. The trend is clear that the use of additional charcoal mass in the reaction mixture actually will decrease the percent yield. This can be attributed to the fact that the additional charcoal adsorbs more of the biodiesel fuel itself, which in turn results in a higher product loss since more biodiesel remains on the charcoal which is disposed of. Therefore, it is concluded that the best yield for deviation 1 can be achieved when no charcoal is added to the mixture.





**Figure 8: Deviation 1 Percent Yield and Water Content vs. Mass Charcoal**

Similarly, the average water content vs. mass of charcoal used in each sample is plotted in Figure 8. The water content of the samples actually increases with the addition of more charcoal mass. However, Table 2 confirms that the water content levels for each sample still fall within the 500 ppm ASTM maximum for samples using 15g of charcoal or less. IR spectra for each run of deviation type 1, like the spectra seen in Figure 9, also confirm the presence of some water in the samples by the noticeable absorption peak at  $3400\text{cm}^{-1}$ . This absorption peak also suggests the presence of methanol in the biodiesel sample. This absorption peak is present in all deviation 1 samples at approximately the same signal strength, suggesting that deviation 1 addition of charcoal does not effectively remove water or methanol from the solution.



**Figure 9: Deviation 1 Representative IR Spectra**

Therefore, it is clear that additional charcoal in this deviation does not effectively reduce water or methanol content in the product. On the contrary, more charcoal in the reaction mixture results in a higher water content and no real effect on methanol content.

Overall, the results of the deviation 1 trials reveal that adding dry charcoal directly to the reaction mixture does not improve the quality of the biodiesel product. Kinematic viscosity confirms that the reaction did take place to a high extent, but the percent yield decreases with additional charcoal while water and methanol content in the product are not affected greatly. This is exactly opposite of the desired result of the additional charcoal addition. Deviation 1 addition of charcoal to the biodiesel reaction mixture is therefore not an effective technique to avoid the need for water wash and water removal steps.

### **Deviation 2: Post Reaction Addition of Charcoal**

In this deviation, various mass charcoal amounts were added to biodiesel fuel samples after they had been prepared by the standard procedure. That is, the charcoal was mixed with the

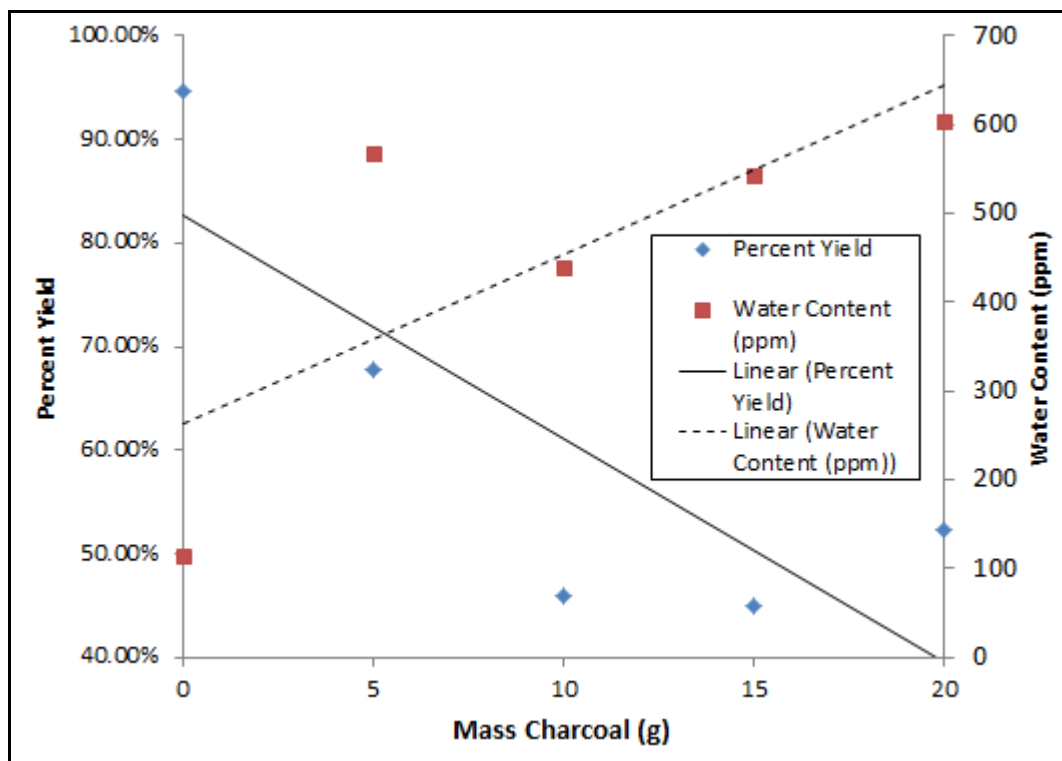
biodiesel fuel product in an attempt to remove any water or methanol remaining in the product. The charcoal was then removed by an additional filtration step. Table 3 summarizes the quality tests conducted on each of the samples synthesized by this method deviation.

**Table 3: Deviation 2 Quality Testing Results**

Mass Charcoal (g)	Percent Yield (from 100mL oil)	Water Content (ppm)	Kinematic Viscosity (cSt)
0.0	95%	115	5.80
5.0	68%	568	6.95
10.0	46%	440	6.65
15.0	45%	543	6.73
20.0	52%	605	6.53

Considering the kinematic viscosities of each sample will allow confirmation that biodiesel fuel product was achieved. The average kinematic viscosities in Table 3 do not fall within the ASTM standard range of 1.9-6.0 cSt, except for the sample made with no charcoal (0 grams). However, the kinematic viscosity of each sample falls just above the upper limit, with each sample having a kinematic viscosity between 6.0-7.0 cSt. Therefore, it can be concluded that each sample was composed of a majority of biodiesel fuel, with limited yet notable amounts glycerol, diglyceride, and triglyceride molecules present in the final product.

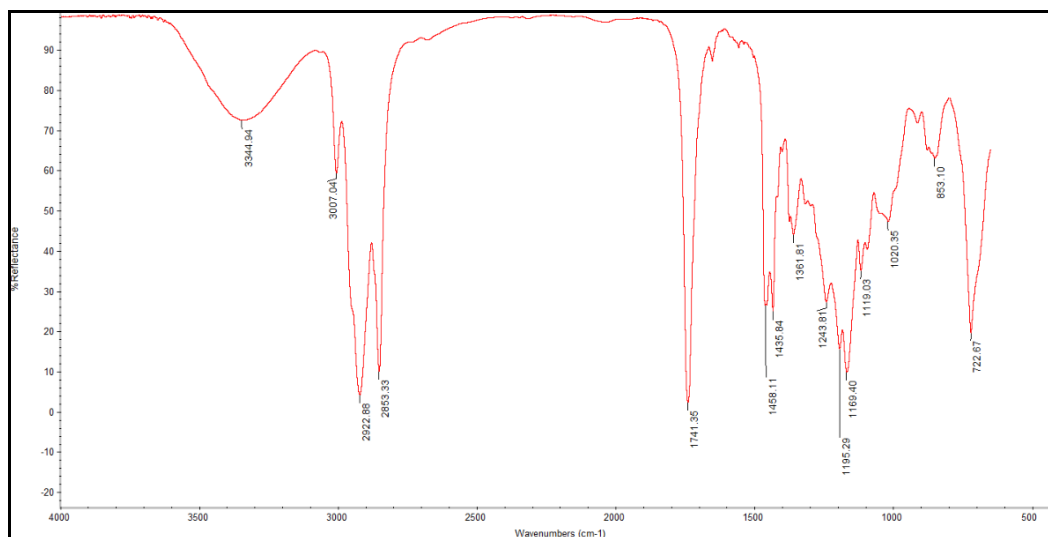
Considering the average percent yield for each run, the trend of decreasing yield with increasing mass of charcoal is again observed. The plot of average yield vs. mass of charcoal used is seen in Figure 10. The trend again shows that the use of additional charcoal will actually decrease the percent yield. This is explained by the loss of biodiesel product due to adsorption to the surface of the increasing amounts of charcoal solids which are being disposed of. Therefore, it is concluded that the best yield for deviation 2 can be achieved when no charcoal is added to the mixture.



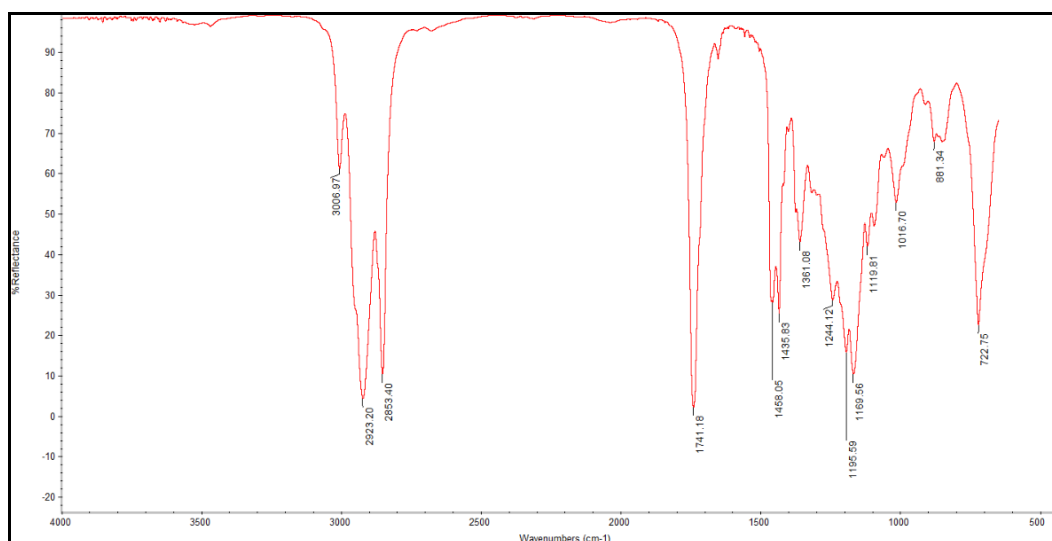
**Figure 10: Deviation 2 Percent Yield and Water Content vs. Mass Charcoal**

The average water content vs. mass of charcoal used in each sample is also plotted in Figure 10. The trend of increasing water content with increasing charcoal mass is again observed. Table 3 confirms that the water content levels increase with increasing charcoal, but still fall within the 500 ppm ASTM maximum for samples using 10g of charcoal or less, with the 15g, and 20g charcoal sample falling just above this maximum.

IR spectra for each run of deviation type 2 show a promising trend. IR spectra confirm that the water and methanol content of the samples actually was decreased by the addition of charcoal. The absorption peak around  $3400\text{cm}^{-1}$  decrease in strength as the mass of charcoal increases. Figure 11 represents the run using 10g of charcoal, while Figure 12 represents the run using 20 g of charcoal.



**Figure 11: Deviation 2, 10g Charcoal IR Spectra**



**Figure 12: Deviation 2, 20g Charcoal IR Spectra**

The absorption peak around  $3400\text{cm}^{-1}$  has clearly decreased in strength as mass of charcoal used has increased. In fact, the “peak” in Figure 12 is almost nonexistent. That is, the deviation 2 sample using 20g of charcoal has almost no methanol or water in it. This sample is very close to matching the biodiesel stock solution IR in Figure 5.

Deviation 2 has shown that the use of a charcoal purification step after the standard biodiesel production procedure does have potential benefits. Though the percent yield of the

product is decreased as mass of charcoal increases, this additional charcoal also corresponds to a decrease in the methanol and water present in the sample, as evidenced by IR spectra. Therefore, the use of charcoal in this way may in fact be an effective alternative to the standard water wash and water removal steps in biodiesel production. Kinematic viscosity confirms that the reaction did take place to a high extent with small yet significant amounts of impurities. It can be concluded that deviation 2 use of a charcoal purification step is a recommended technique for further investigation and costing analysis, given that it could eliminate the need for water wash and water removal steps, but at the cost of a decreasing percent product yield.

### **Deviation 3: Coating Charcoal with NaOH**

In this deviation, the desired mass of NaOH (approximately 0.350g) was coated on charcoal samples of varying mass amounts. The NaOH coated charcoal was then added to the methanol to create the pre-reaction broth, which was then added to the heated oil to initiate the reaction. The charcoal was filtered out after the reaction upon transfer to the separatory funnel. Table 4 summarizes the quality tests conducted on each of the samples synthesized by this method.

**Table 4: Deviation 3 Quality Testing Results**

Mass Charcoal (g)	Percent Recovery (from 100mL oil)	Water Content (ppm)	Kinematic Viscosity (cSt)
0.0	95%	115	5.80
5.0	85%	157	27.30
10.0	76%	198	26.79
15.0	65%	283	24.60

In considering this data, the kinematic viscosity numbers raise immediate concern. The samples which used charcoal in any amount (the zero gram sample is the base case biodiesel standard) had kinematic viscosity values of approximately 26.0 cSt. This is significantly above

the ASTM standard range of 1.9-6.0 cSt. Therefore, it is concluded that the samples produced by this deviation are in fact not biodiesel fuel. The samples likely contain high fractions of unconverted triglyceride or diglyceride molecules, leading to the high viscosity values.

This low conversion to the biodiesel fuel product can be attributed to the fact that the NaOH and methanol did not have sufficient time or means to form the aqueous sodium methylate mixture. Normally, this mixture is created in the absence of charcoal. However, in this deviation, the charcoal was present in the pre-reaction broth (the NaOH was introduced to the broth by being coated on charcoal). It is believed that the presence of charcoal interfered with the production of the aqueous sodium methylate. Therefore, the extent of the transesterification reaction was decreased because the sodium methylate was not present in significant enough amounts. An additional cause of the observed low conversions is that not all of the NaOH may have been coated on the charcoal sample, such that there was not enough NaOH in the pre-reaction broth. This would prevent the transesterification from occurring if not enough sodium hydroxide were present in the mixture to catalyze the reaction.

Overall, deviation 3 trials have shown that this particular method is not effective for producing biodiesel fuels. The method's effect on yield and water content was not evaluated since the samples produced were not in fact biodiesel fuels. Therefore, deviation 3 is not recommended for further study or use as it has proven to be an ineffective technique.

#### **Deviation 4: Coating Charcoal with NaOMe**

In deviation 4, the pre-reaction broth of NaOH and methanol was mixed and stirred as usual, and then charcoal was added to this mixture. The mixture was put in the heating chamber to evaporate the liquid, theoretically coating the charcoal with sodium methylate. This coated charcoal was then added directly to the hot oil to initiate the reaction. The charcoal was filtered

out after the reaction upon transfer to the separatory funnel. Table 5 summarizes the quality tests conducted on each of the samples synthesized by this method.

**Table 5: Deviation 4 Quality Testing Results**

Mass Charcoal (g)	Percent Recovery (from 100mL oil)	Water Content (ppm)	Kinematic Viscosity (cSt)
0.0	95%	115	5.80
5.0	78%	120	35.48
10.0	69%	75	35.60
15.0	63%	51	35.03

The kinematic viscosity data here shows that there was almost no conversion of the oil to the desired biodiesel products. The viscosity values here are approximately 35.0 cSt, which is way above the ASTM standard for biodiesel fuels. Additionally, this matches the measured viscosity values of the canola oil reactant material, which was approximately 36.0 cSt. Therefore, it can be concluded that almost no conversion of the oil occurred in the deviation 4 trials.

The fact that essentially no biodiesel was produced suggests that sodium methylate was not in fact coated on the charcoal as was intended. When the pre-reaction broth was mixed with the charcoal and then evaporated, it is likely that the methanol simply evaporated leaving only the NaOH behind to be coated on the charcoal. As a result, only NaOH was added to the oil during the reaction, without any methanol or sodium methylate. In the absence of either of these, it is absolutely impossible for the transesterification reaction to occur. Therefore, this explains the lack of any conversion of the oil to biodiesel fuel.

In conclusion, deviation 4 is certainly not an effective approach to producing biodiesel fuel. A nearly zero percent conversion of the oil was observed, indicating that the method here is useless. It was recognized that excess methanol must be added to the reaction mixture in order for the reaction to proceed, and coating the charcoal with sodium methylate results in the evaporation



of any excess methanol that would be added to the reaction mixture. Thus, any additional trials of deviation 4 are not recommended.

## Chapter 5

### Conclusions and Recommended Next Steps

Overall, it has been seen that the use of charcoal as an additive in biodiesel production can provide synthesis benefits, but only in particular applications. Various deviations to the standard biodiesel synthesis procedure were investigated to determine the best amount and best step in the procedure to add activated charcoal to the reaction mixture.

Deviations 1 shows that the addition of activated charcoal directly to the reaction mixture was not an effective alternative to the standard water wash and water removal steps. Additional charcoal mass decreased product yield and increased water content in the product, while having little effect on the presence of methanol in the product.

On the other hand, deviation 2 did show promising results. Mixing standard biodiesel samples with charcoal to attempt to remove remaining methanol and water in solution proved to be an effective technique. Additional charcoal mass resulted in a decrease in overall methanol and water contained in the sample, as evidenced by IR spectra for the samples. However, increased charcoal mass did decrease the product percent yield due to loss of product adsorbed to the charcoal. It is recommended that deviation 2 be investigated further, including a cost analysis to determine the tradeoff between the benefits of using charcoal as a purification step versus the cost of the lost biodiesel product as charcoal mass increased.

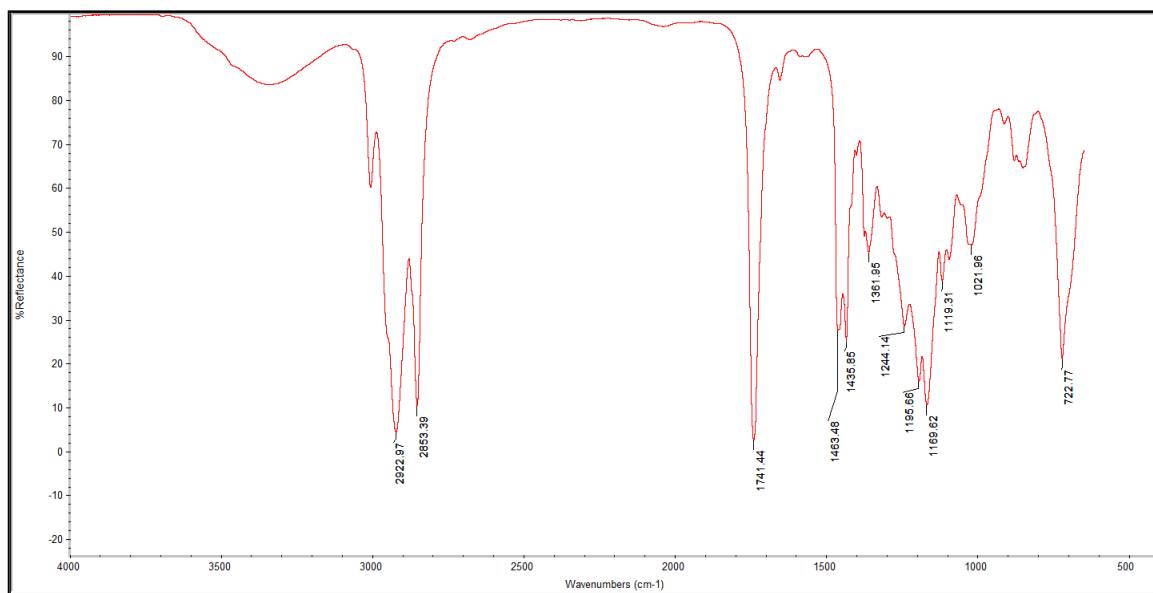
Deviations 3 and 4 attempt to introduce the NaOH and sodium methylate to the reaction mixture by coating these solids onto the surface of the charcoal. In both of these cases, the result is a very low conversion to the biodiesel product. That is, kinematic viscosity values prove that almost no biodiesel fuel was synthesized. Therefore, neither of these deviations are recommended for further consideration since the primary objective of synthesizing biodiesel fuel was not met.

With all of these things in mind, it can be concluded that the use of activated charcoal as a purification step may be an effective alternative to the standard water wash and water purification steps. That is, the use of charcoal in the purification steps following the synthesis reaction itself (Deviation 2) has been demonstrated as an effective technique. However, the use of charcoal as a component either before or during the transesterification reaction itself (Deviations 1, 3, and 4) was demonstrated to be ineffective in all cases.

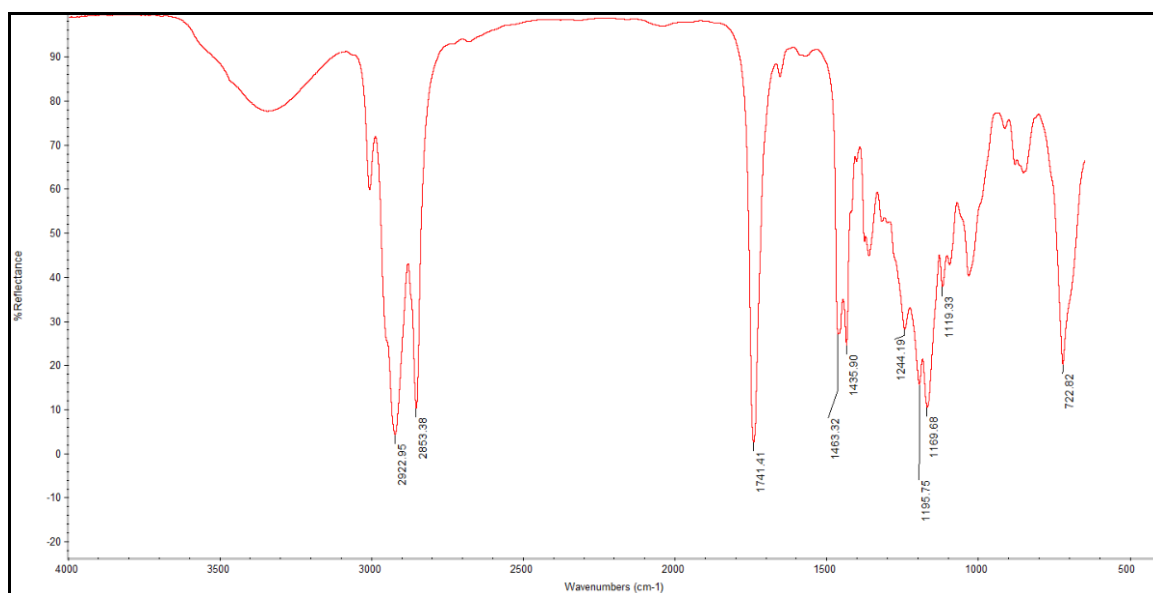
Further research and testing pertaining to deviation 2 is recommended. In particular, a cost analysis should be conducted by employing a much larger sample size (using charcoal mass increments smaller than 5.0g) and determining the optimum percent product loss versus the biodiesel fuel composition. Overall, deviation 2 use of solid charcoal potentially eliminates the need for any water wash or water removal steps, so a cost analysis should be performed to determine feasibility. Overall, it appears that the use of activated charcoal as a resource in biodiesel fuel production is effective as a purification step, but not as a reaction step.

## Appendix A

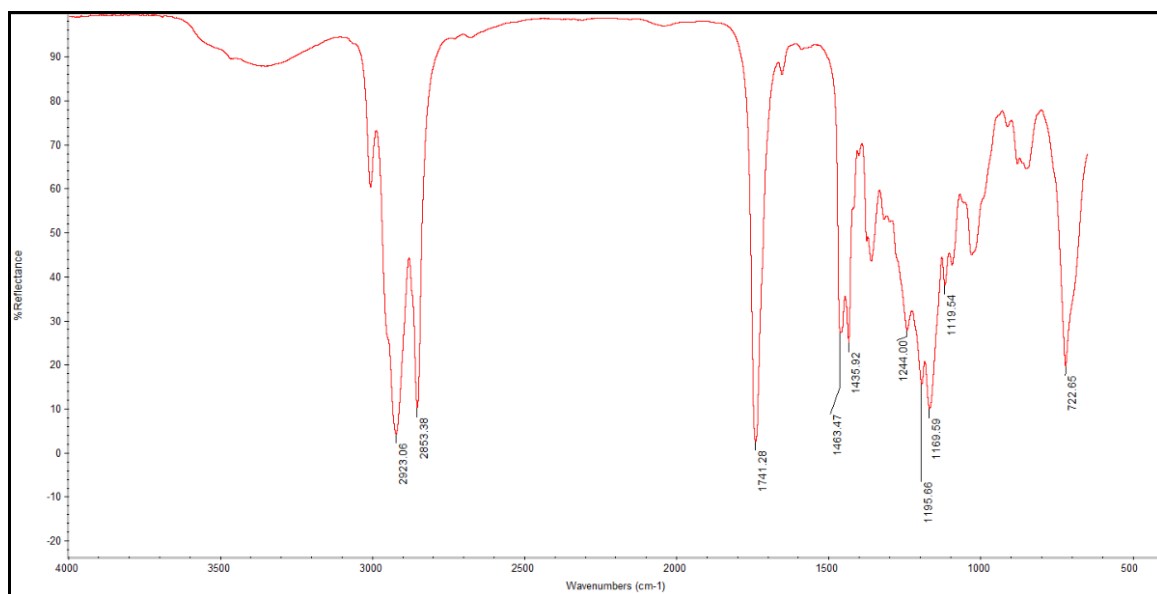
### FTIR Spectra for all Samples



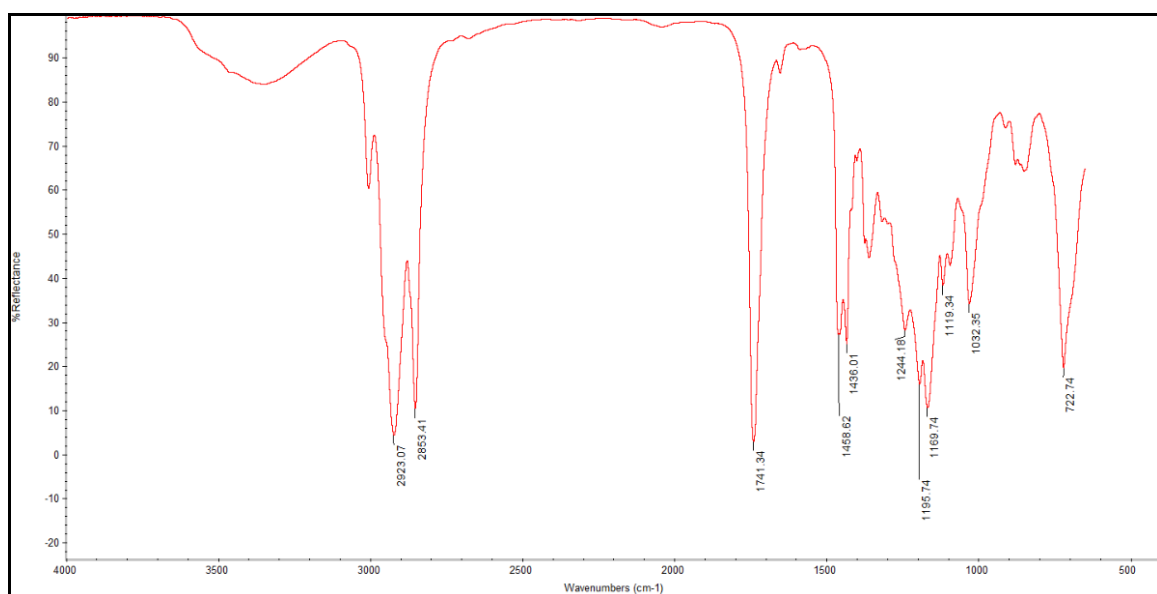
Run 1: Standard Procedure Trial 1



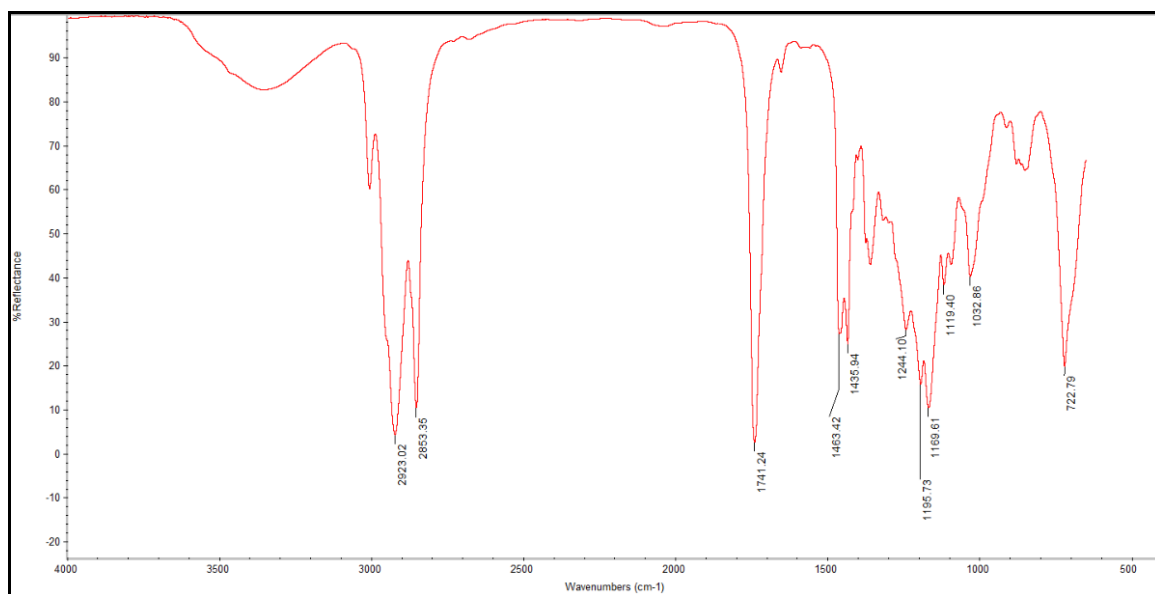
Run 2: Standard Procedure Trial 2



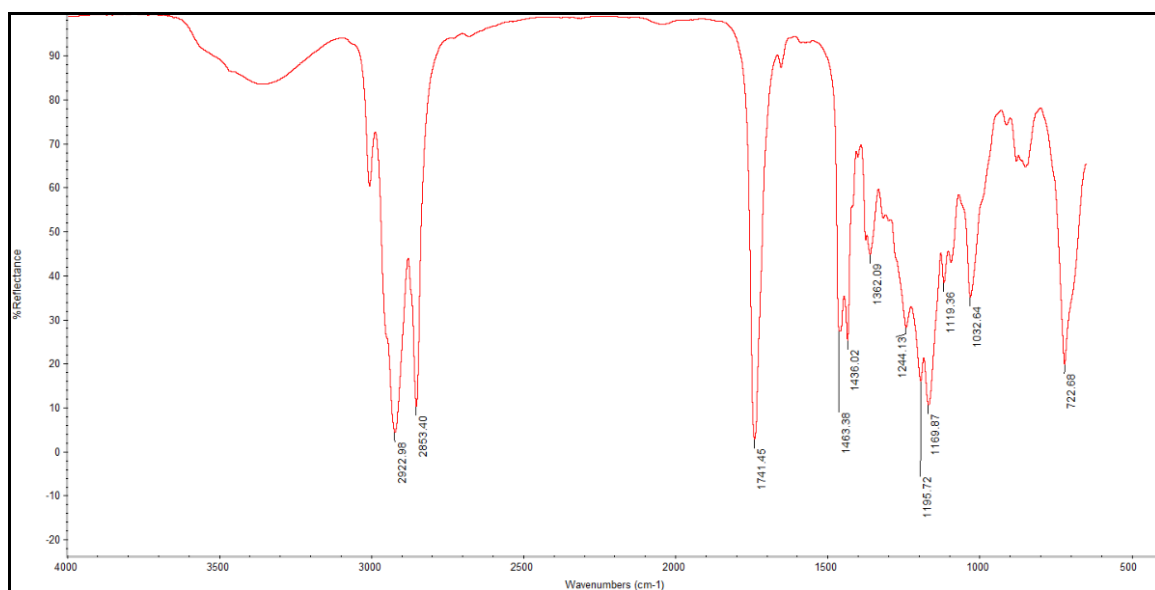
**Run 3: Deviation 1, 5g charcoal, Trial 1**



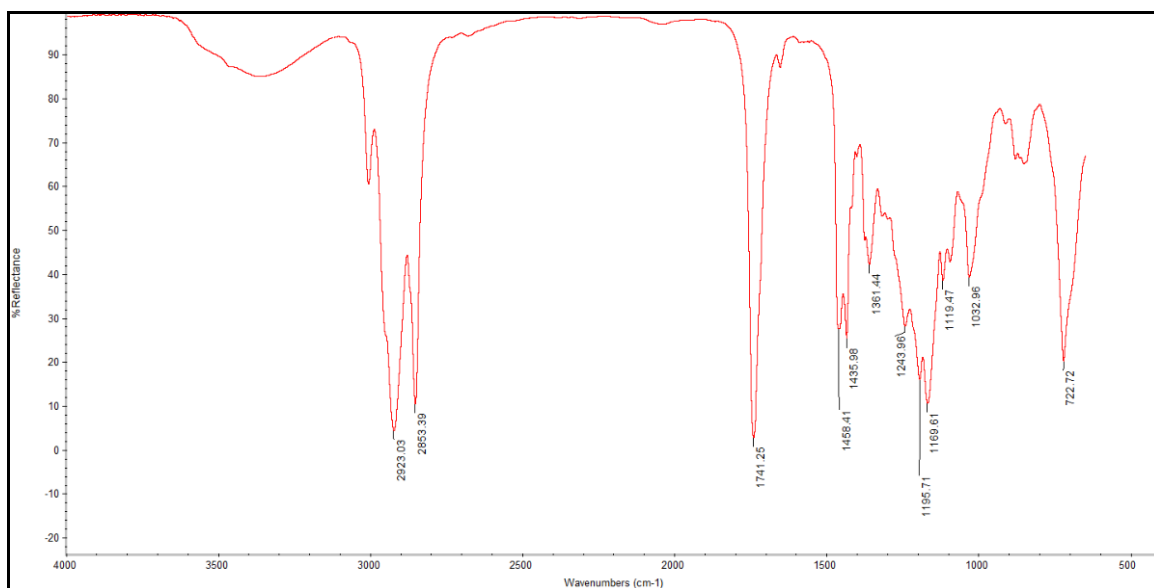
**Run 4: Deviation 1, 5g charcoal, Trial 2**



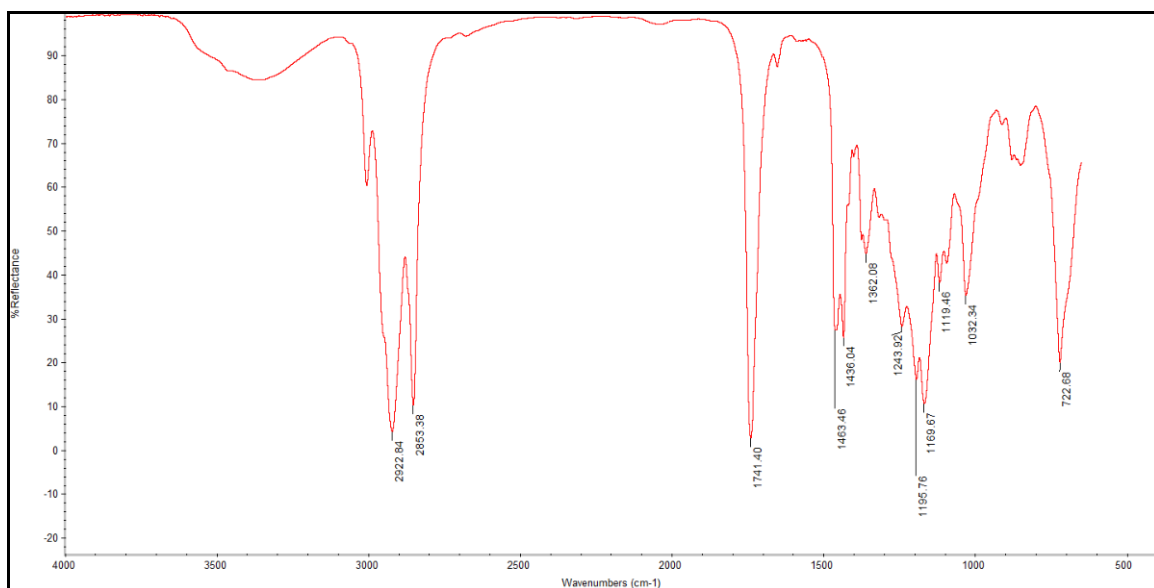
**Run 5:** Deviation 1, 10g charcoal, Trial 1



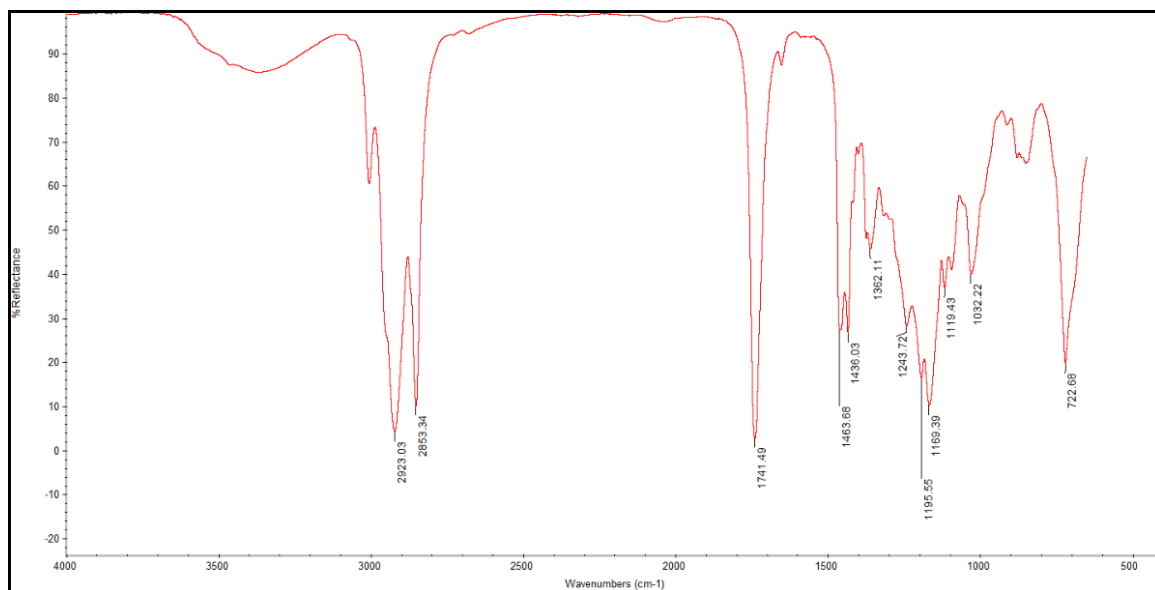
**Run 6:** Deviation 1, 10g charcoal, Trial 2



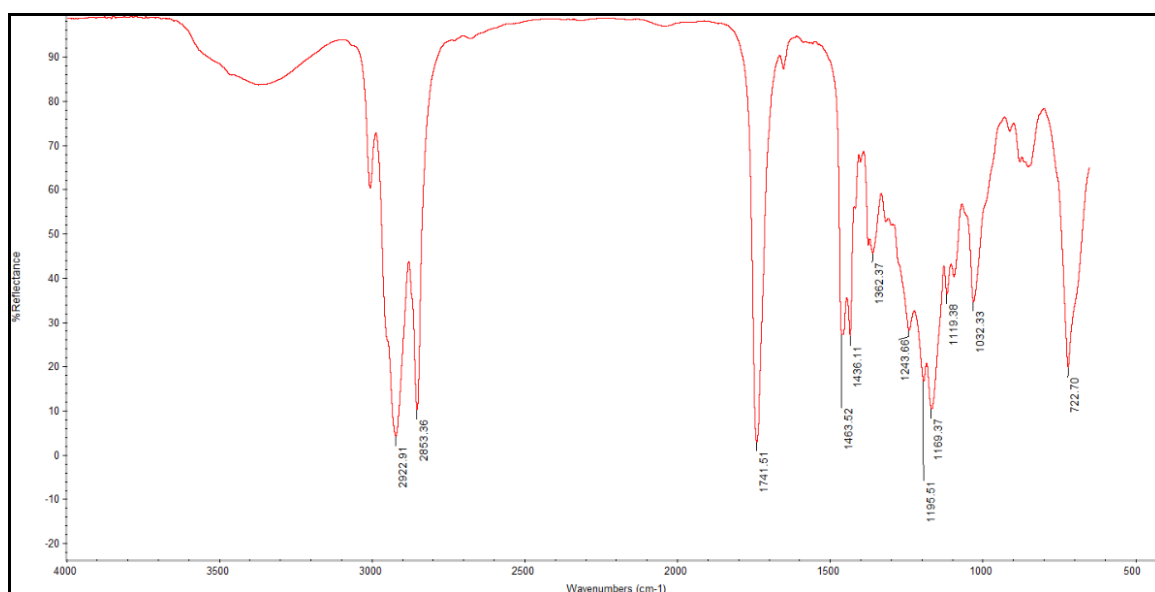
**Run 7:** Deviation 1, 15g charcoal, Trial 1



**Run 8:** Deviation 1, 15g charcoal, Trial 2

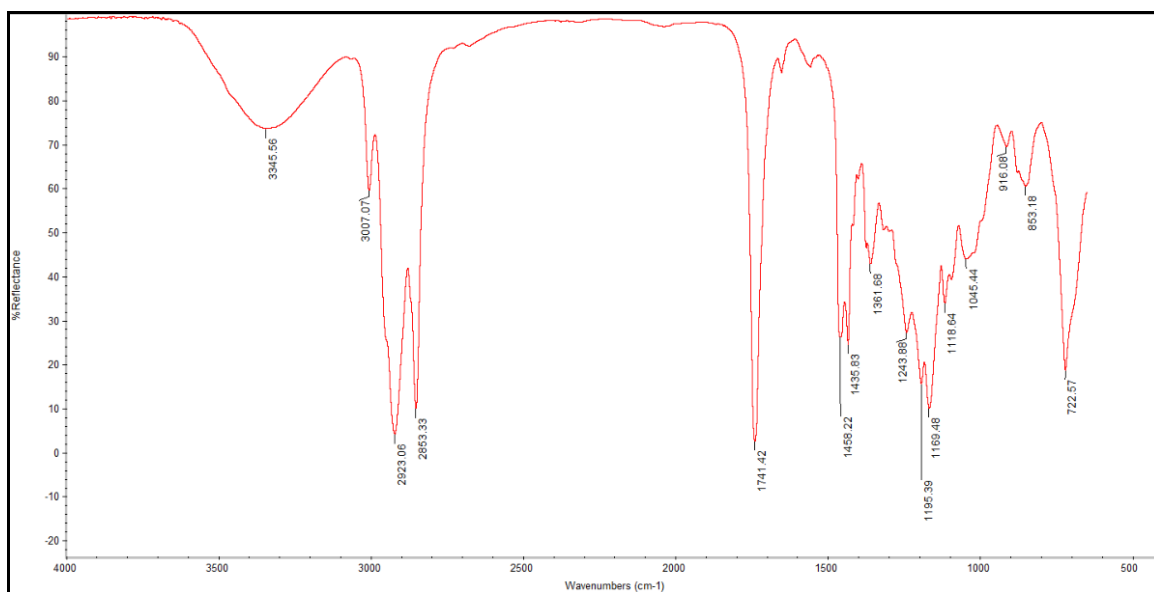


**Run 9:** Deviation 1, 20g charcoal, Trial 1

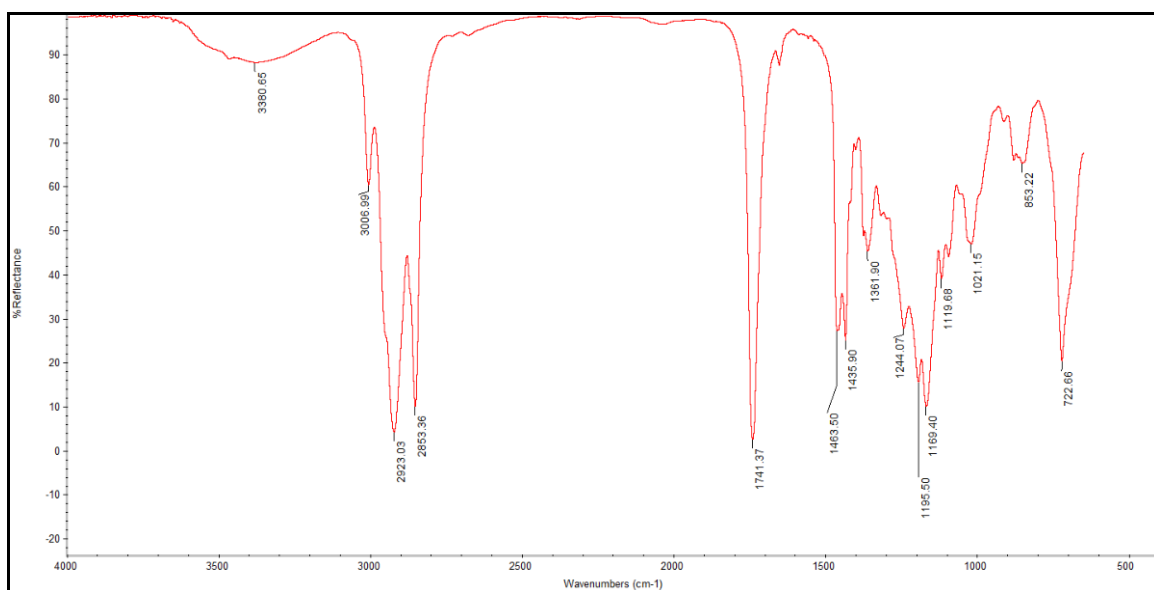


**Run 10:** Deviation 1, 20g charcoal, Trial 2

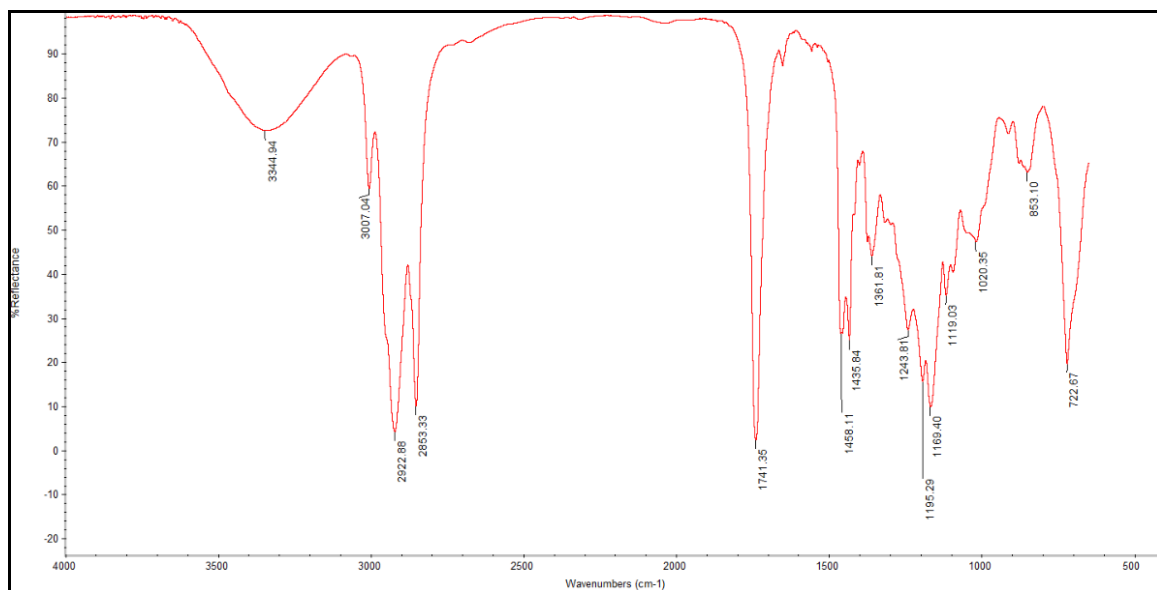




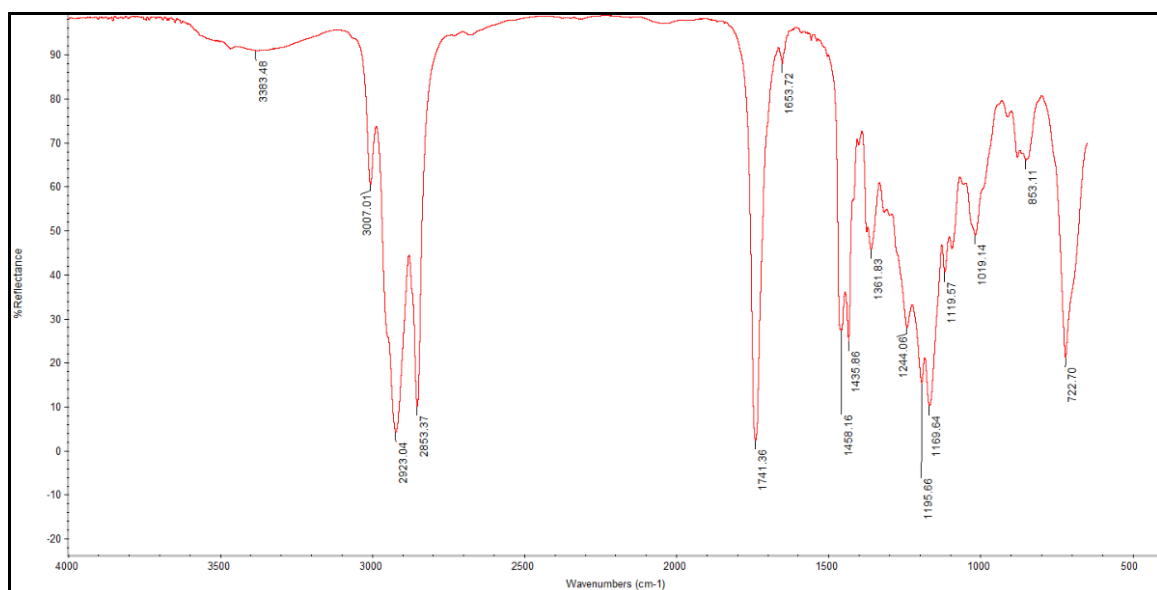
**Run 11: Deviation 2, 5g charcoal, Trial 1**



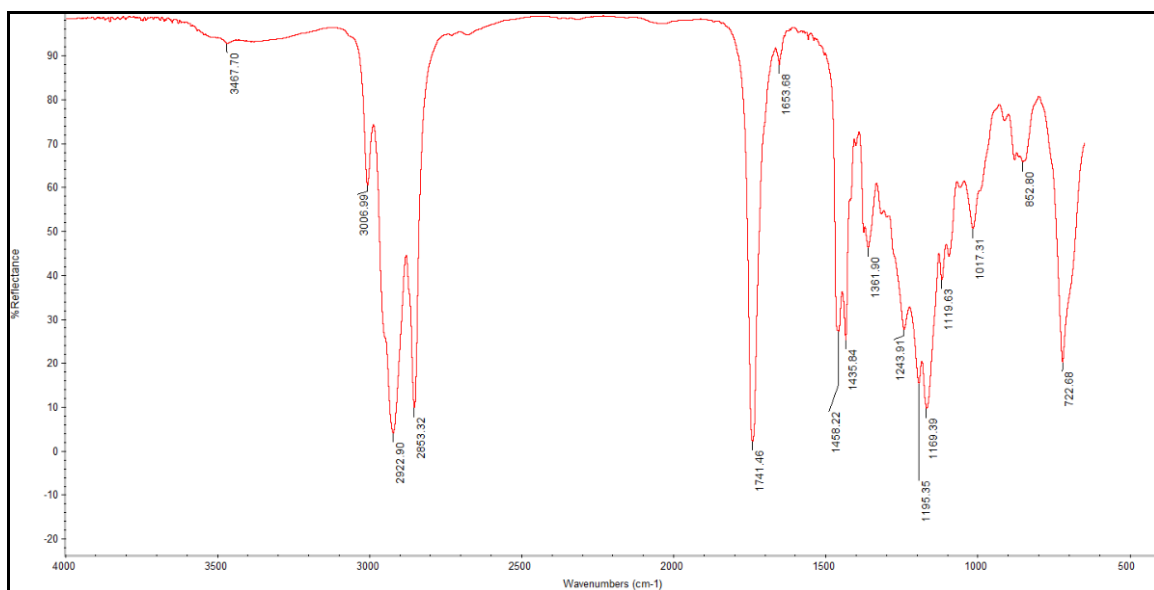
**Run 12: Deviation 2, 5g charcoal, Trial 2**



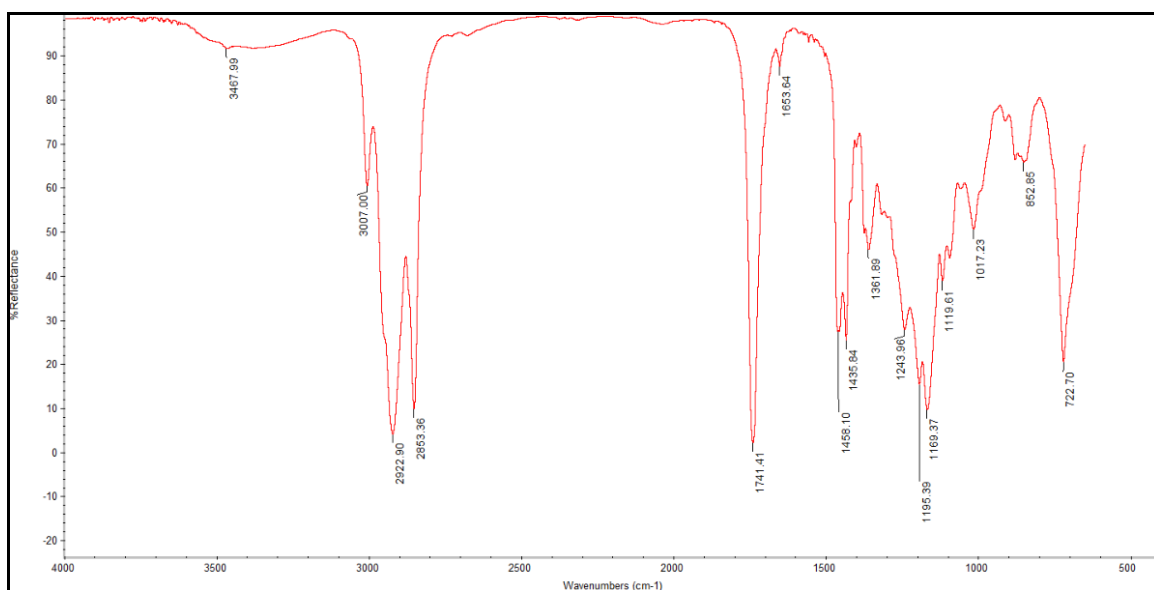
**Run 13: Deviation 2, 10g charcoal, Trial 1**



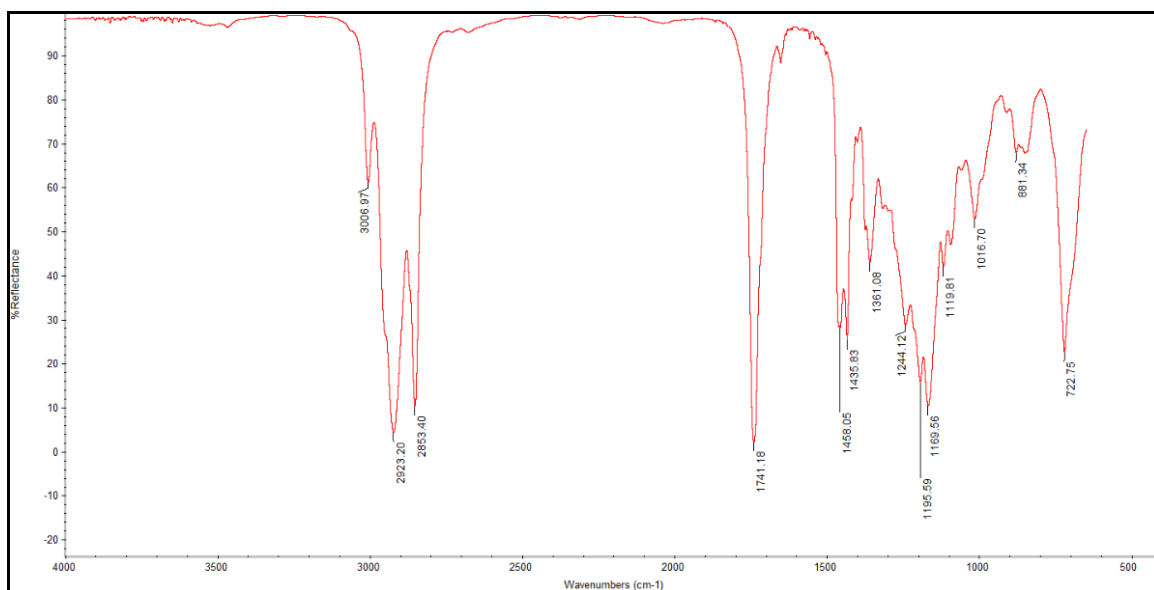
**Run 14: Deviation 2, 10g charcoal, Trial 2**



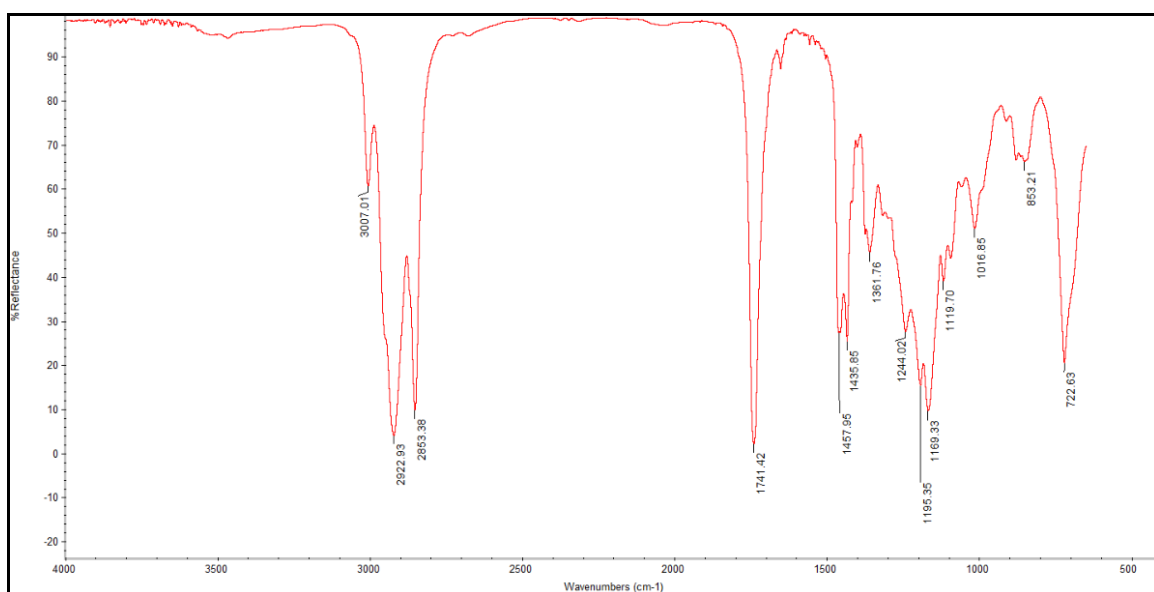
**Run 15: Deviation 2, 15g charcoal, Trial 1**



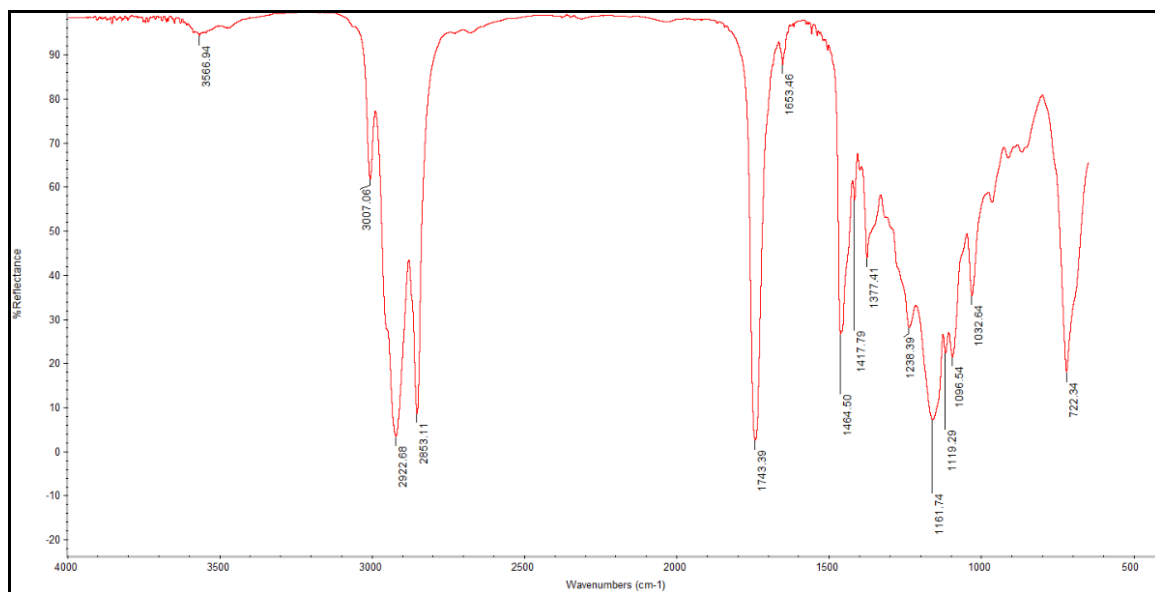
**Run 16: Deviation 2, 15g charcoal, Trial 2**



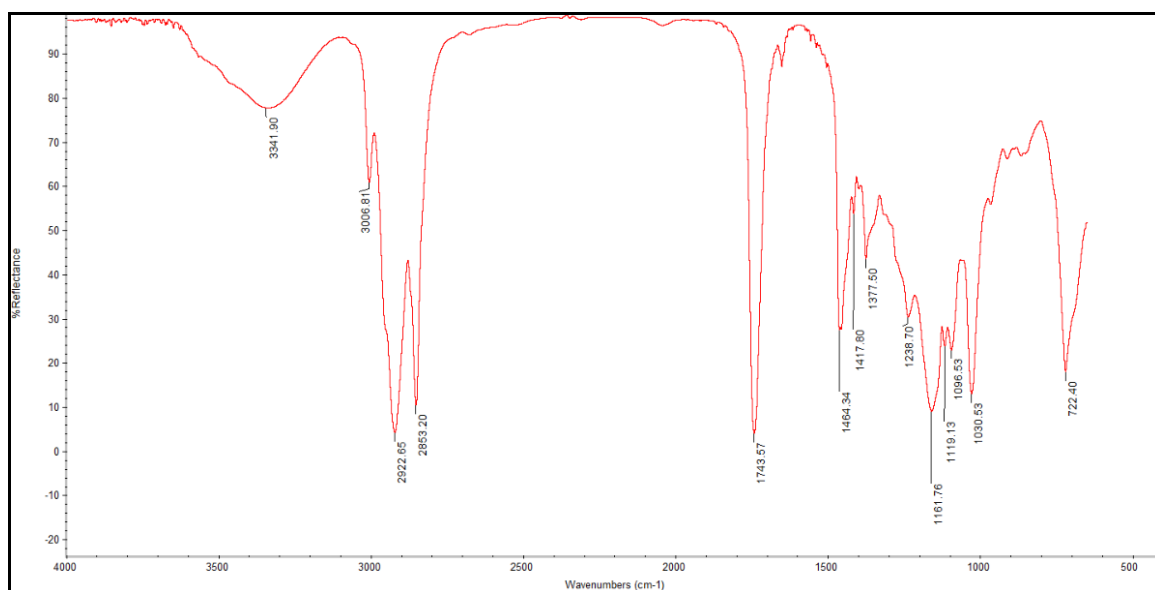
**Run 17: Deviation 2, 20g charcoal, Trial 1**



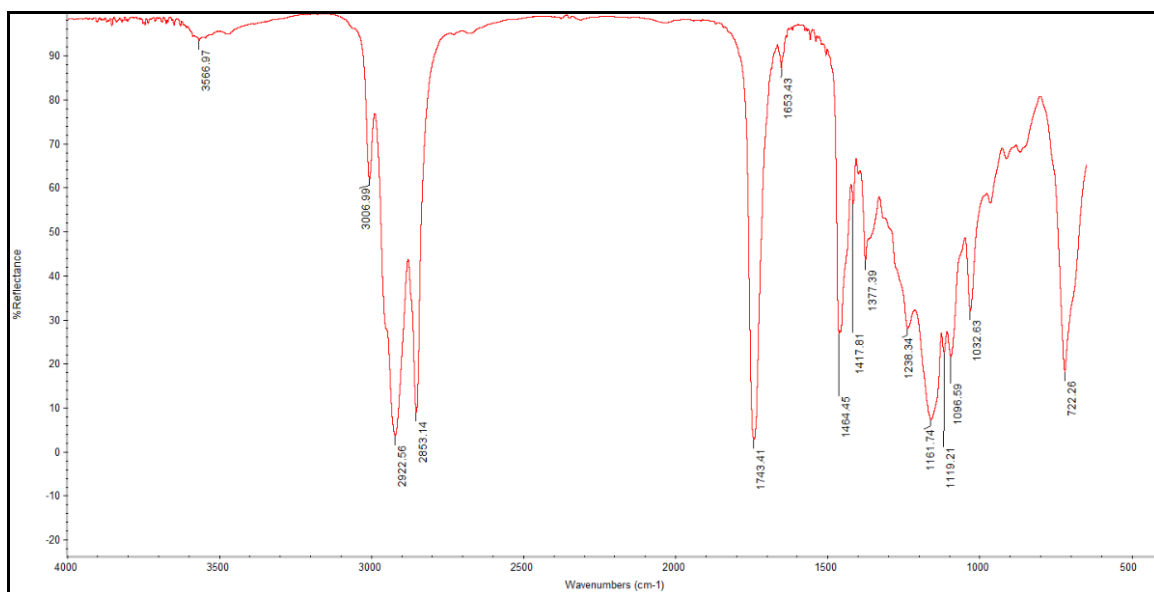
**Run 18: Deviation 2, 20g charcoal, Trial 2**



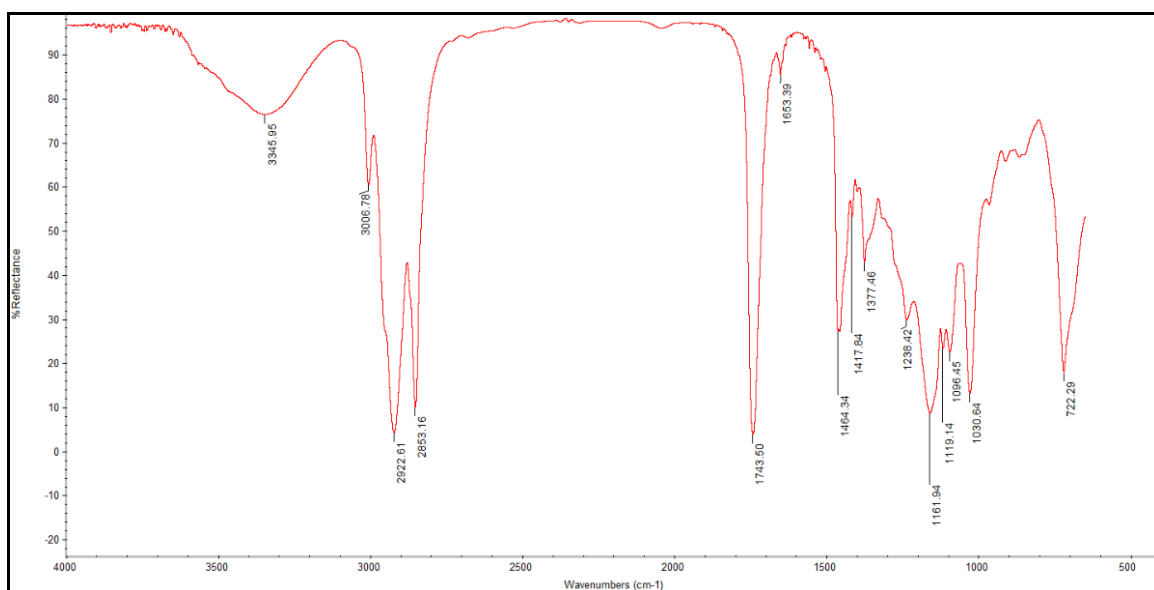
**Run 19:** Deviation 3, 5g charcoal, Trial 1



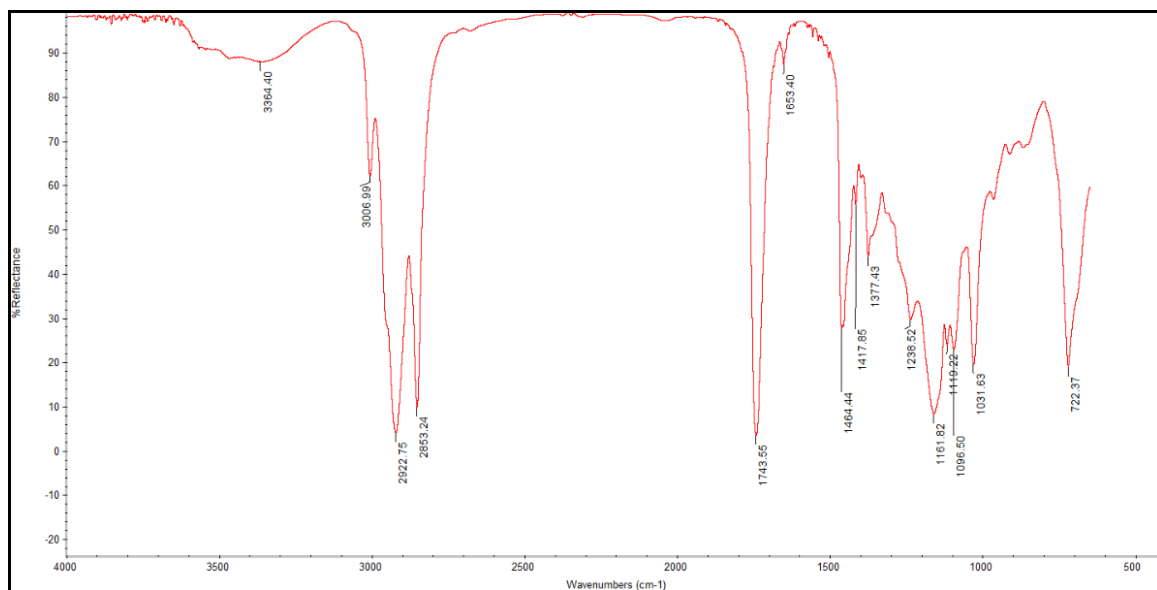
**Run 20:** Deviation 3, 5g charcoal, Trial 2



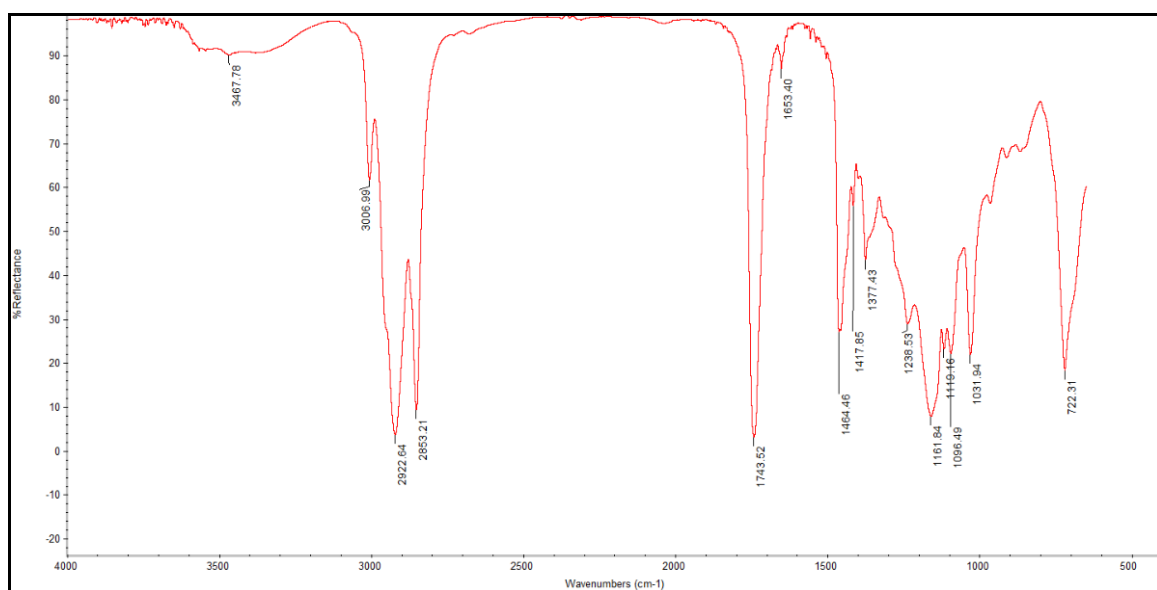
**Run 21: Deviation 3, 10g charcoal, Trial 1**



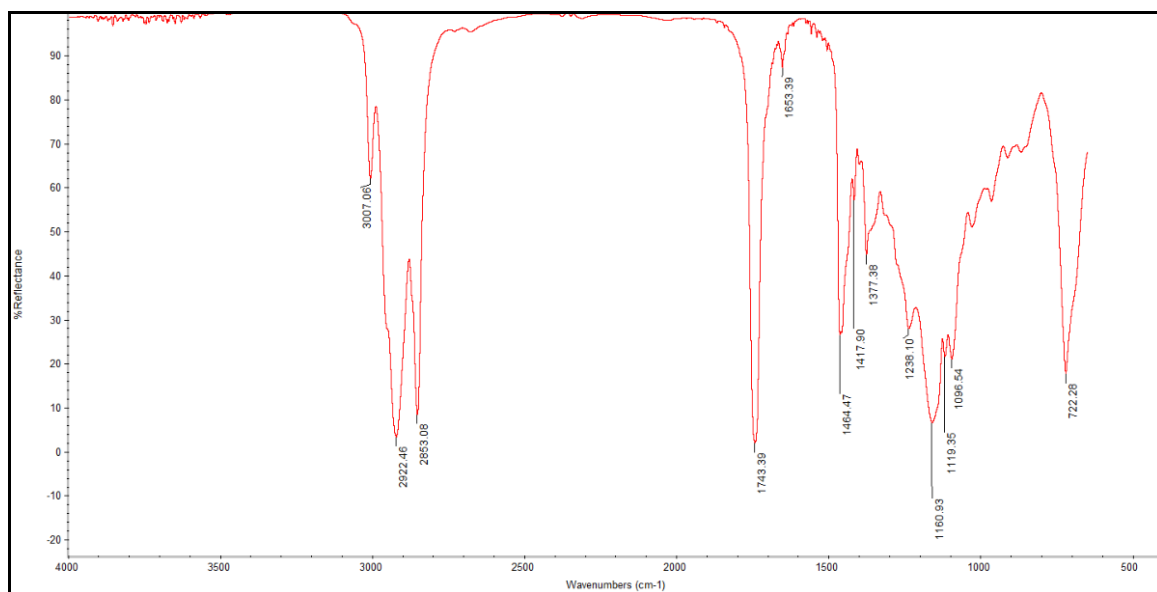
**Run 22: Deviation 3, 10g charcoal, Trial 2**



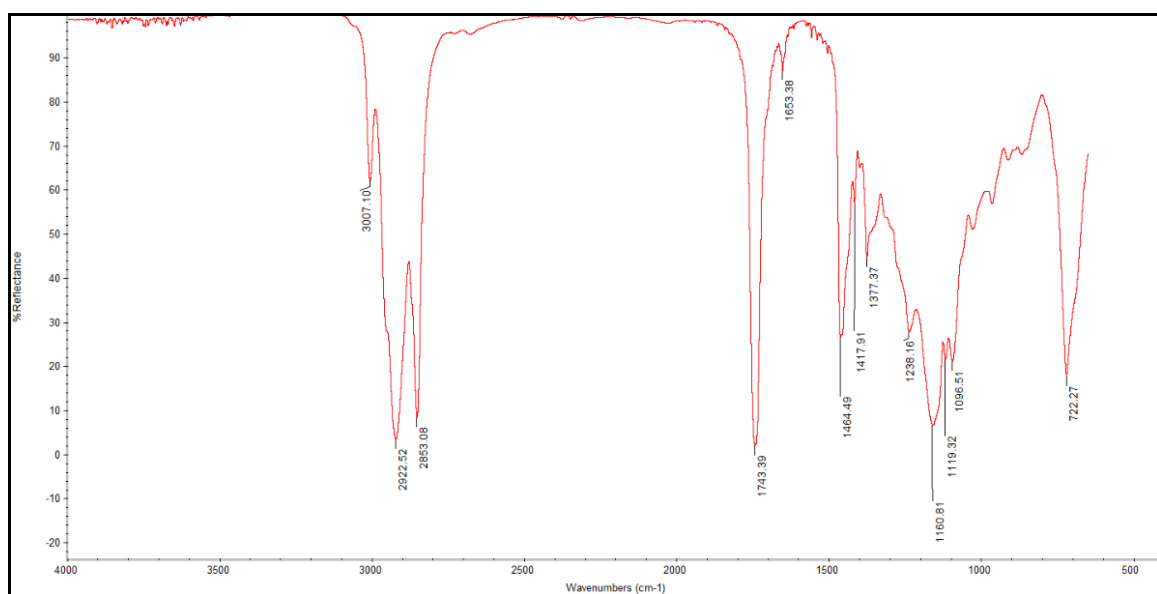
**Run 23:** Deviation 3, 15g charcoal, Trial 1



**Run 24:** Deviation 3, 15g charcoal, Trial 2

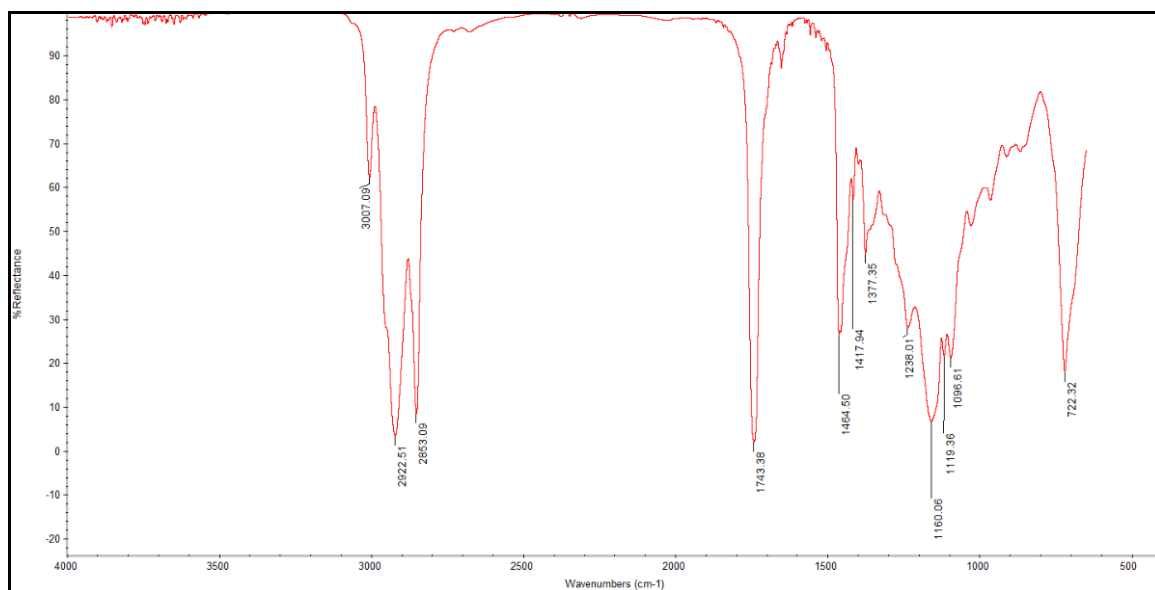


**Run 27:** Deviation 4, 5g charcoal, Trial 1

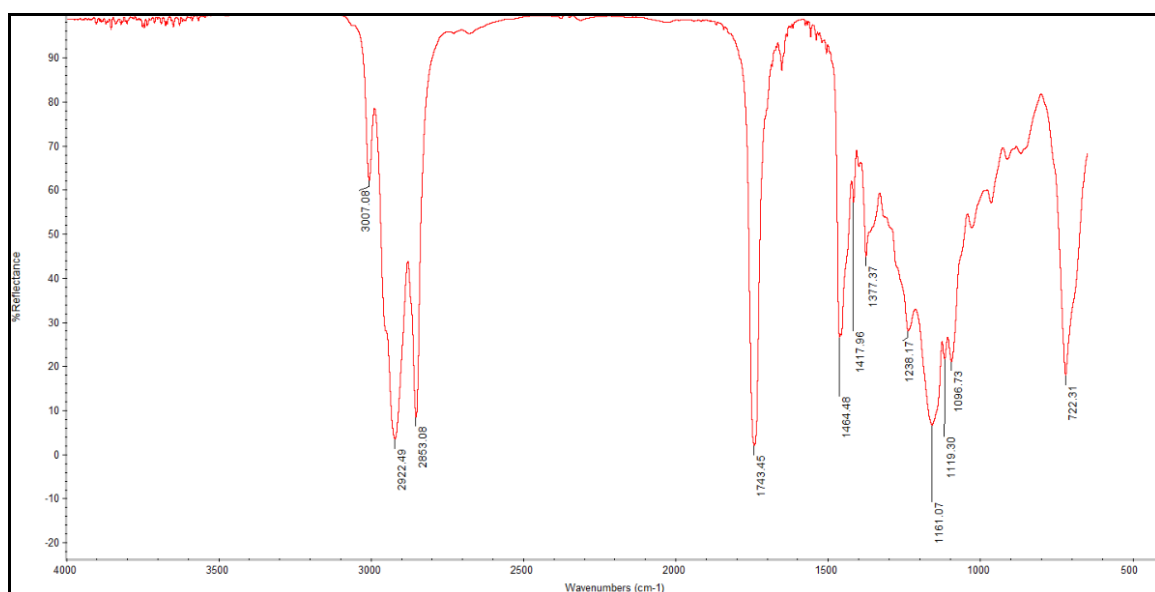


**Run 28:** Deviation 4, 5g charcoal, Trial 2

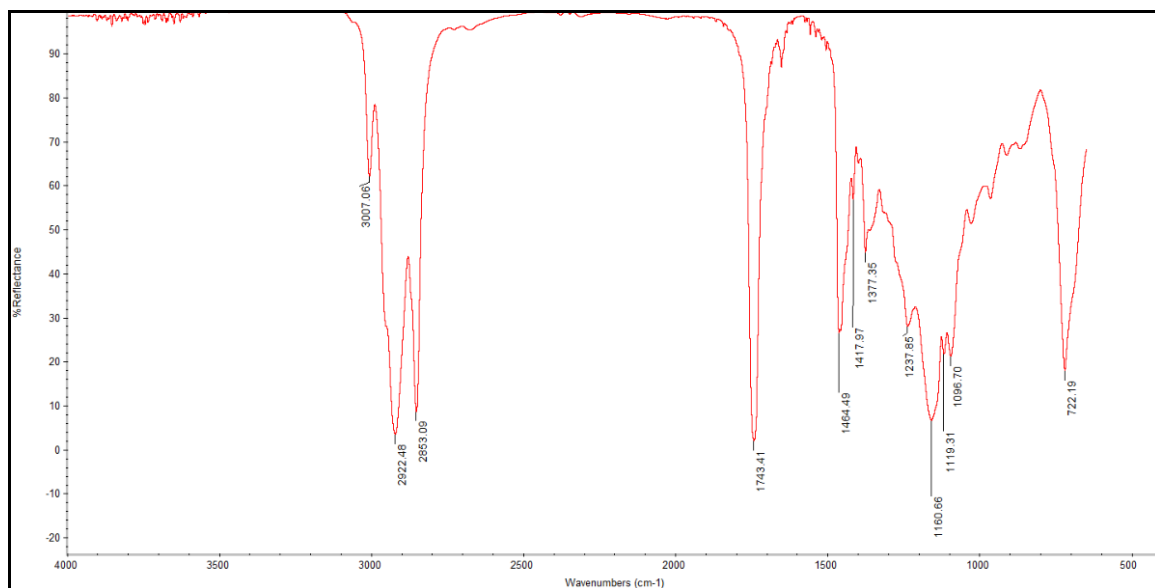




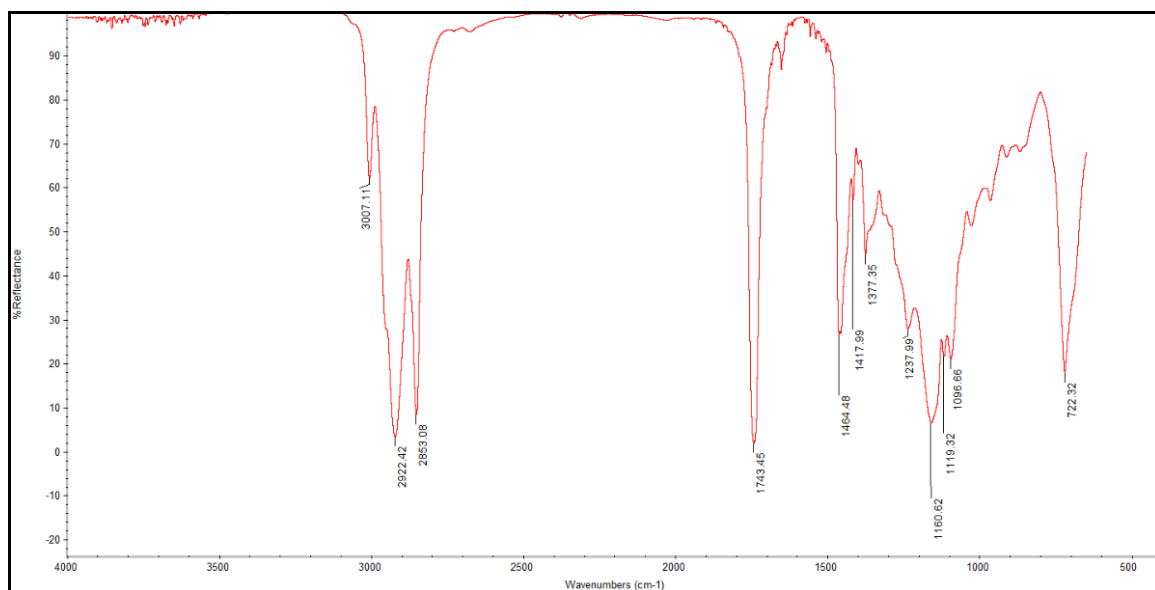
**Run 29:** Deviation 4, 10g charcoal, Trial 1



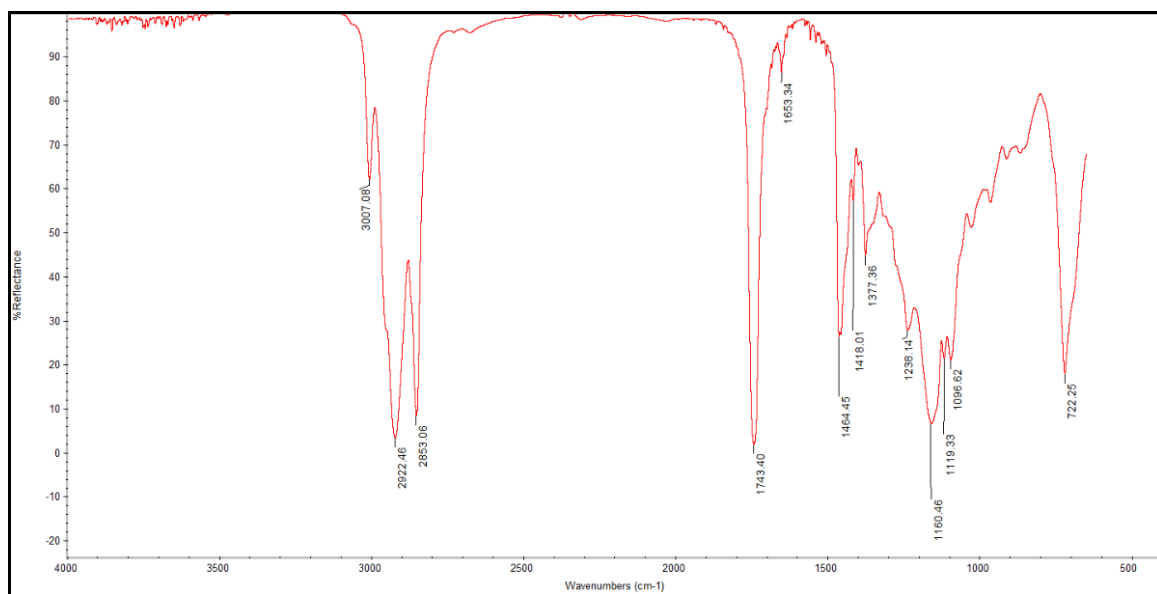
**Run 30:** Deviation 4, 10g charcoal, Trial 2



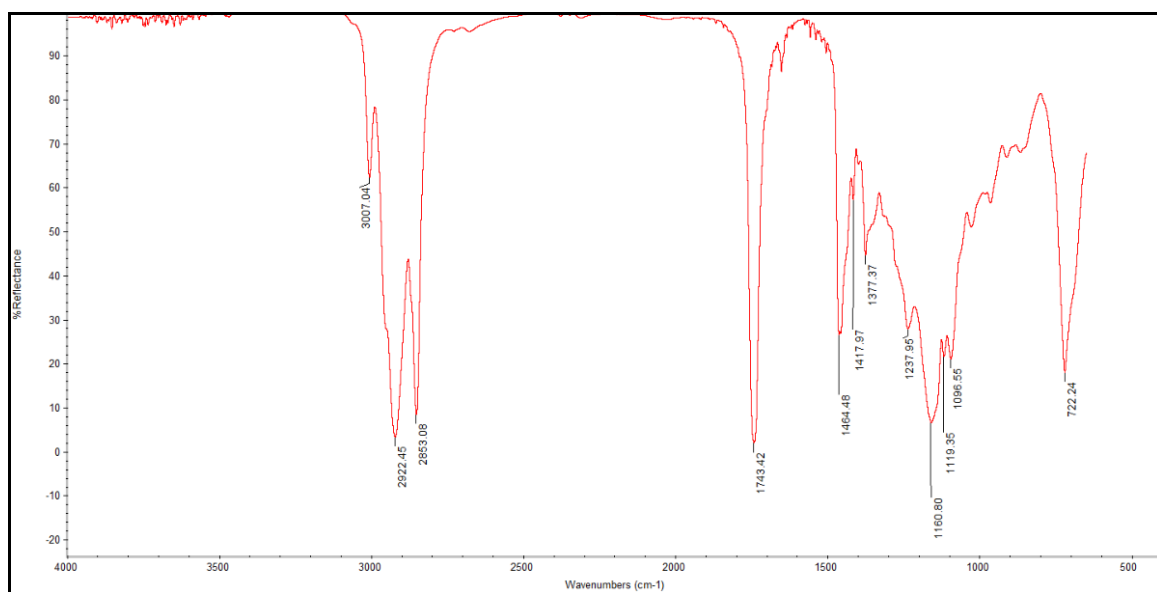
**Run 31: Deviation 4, 15g charcoal, Trial 1**



**Run 32: Deviation 4, 15g charcoal, Trial 2**



**Run GV: Great Value Canola Oil Standard**



**Run WEIS: WEIS Canola Oil Standard**

## Appendix B

### Lab Data Table

Grams Charcoal	Charcoal Introduced	Mass Charcoal (g)	Percent Yield (from 100mL oil)	Water Content (ppm)	Kinematic Viscosity (cSt)
<b>Biodiesel Standard</b>					
0	BD Standard	0.0	94.73%	115	5.80
<b>Deviation 1</b>					
0	BD Standard	0.0	95%	115	5.80
5	in rxn mixture	5.0	84%	209	6.02
10	in rxn mixture	10.0	77%	240	5.89
15	in rxn mixture	15.0	65%	394	6.01
20	in rxn mixture	20.0	55%	546	6.99
<b>Deviation 2</b>					
0	BD Standard	0.0	95%	115	5.80
5	after glycerol sep	5.0	68%	568	6.95
10	after glycerol sep	10.0	46%	440	6.65
15	after glycerol sep	15.0	45%	543	6.73
20	after glycerol sep	20.0	52%	605	6.53
<b>Deviation 3</b>					
0	BD Standard	0.0	95%	115	5.80
5	pre-methanol	5.0	85%	157	27.30
10	pre-methanol	10.0	76%	198	26.79
15	pre-methanol	15.0	65%	283	24.60
<b>Deviation 4</b>					
0	BD Standard	0.0	95%	115	5.80
5	into liq mix, evap	5.0	78%	120	35.48
10	into liq mix, evap	10.0	69%	75	35.60
15	into liq mix, evap	15.0	63%	51	35.03
<b>Canola Oil Standards</b>					
Great Value Oil Standard		NA	NA	54	35.93
WEIS Oil Standard		NA	NA	193	37.15

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8. "Activated Charcoal Universal Antidote." EMR Labs, LLC., 2 March 2014. Web. <<http://www.quantumbalancing.com/activatedcharcoal.htm>>.

# ACADEMIC VITA

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Evan Pugh Senior Scholar Award (2014)  
Evan Pugh Junior Scholar Award (2013)  
President Spark Award (2012)  
President's Freshman Award (2011)  
Eagle Scout Award—Boy Scouts of America (2006)

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<b>Finance Captain</b> , Penn State Dance Marathon	(2013-2014)
<b>Instrumentalist</b> , Penn State Blue Band	(2010-2014)
<b>Member</b> , OXE (Chemical Engineering Honors Society)	(2012-2014)
<b>Morale Committee Member</b> , Penn State Dance Marathon	(2011-2012)
<b>OPPerations Committee Member</b> , Penn State Dance Marathon	(2010-2011)

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<b>Engineering Tutor</b> , PSU Tutoring Center (AEC), State College PA	Spring 2012-Fall 2013
<b>Student Assistant</b> , PSU Engineering Advising Center, State College PA	Summer 2012