THE DEHYDRATION AND ODOR TREATMENT OF FUSEL AND ITS APPLICATIONS FOR INSTANT LIGHT CHARCOAL BRIQUETTES

by

JESSICA HORN

(Under the Direction of JASON LOCKLIN)

ABSTRACT

This work aims to explore the use of an alternative to petroleum for ignition of charcoal briquettes. Fusel was chosen for this study as it is a low cost by-product of bioethanol production and has a high concentration of long chain alcohols as an ignition source. Fusel was first dehydrated using crude glycerin, a waste product of biodiesel production, to lower water content below three percent. Next odor treatments were employed to remove the distinct odor of fusel, likely caused by the presence of butyric acid. Among the treatments were active carbon and transesterification of butyric acid. For the charcoal briquettes, factors such a loading and evaporation were considered among three different briquette types. Once the briquette and loading procedure were finalized, bagging test were conducted in the context of a heat sealed single and multiple use bag. Both were successful at atmosphere exposure times under one hour.

INDEX WORDS: FUSEL, GYLCERIN, CHARCOAL, BIODESIEL, INSTANT LIGHT BRIQUETTES

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DEDICATION

To my family. Thank you for all your love and support over the years. You have been nothing but supportive from the very beginning in helping me achieve my dreams. Without your strength and support, I would not be the person I am today.

To Mac Wallace, throughout this process you have been by my side every step of the way as my rock and my cheering squad. You have never once let me doubt myself and whenever those thoughts creep in you are quick to banish them. The encouragement and the support I have received is what truly made this all possible.

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CHAPTER 1

INTRODUCTION

Charcoal is one of the more popular cooking methods around the world. It offers advantages over wood fires with less smoke and more heat per quantity[1]. It is commonly used in backyard barbeques and by street vendors. However, there has been interest in impact these cooking fumes have on human health. Cooking fumes are known to contain substances with mutagenic activity, such as heterocyclic amines[2], and polycyclic aromatic hydrocarbons[3]. There is ample evidence that cooking fumes are associated with an increased risk of respiratory tract cancer in chefs, bakers, and other foodservice workers[4]. One study of barbeque charcoal from 4 Asian countries found benzene and toluene were the most abundant volatile organic compounds (VOCs) emitted along with carbonyl compounds, like formaldehyde[5]. Due to the health risks associated with these petroleum compounds, there was a desire to create a bio-based alternative for the burning of charcoal.

Fusel and Biodiesel

One source for bio-based ignitable materials was found in the production of bioethanol. This process generates a multiple alcohol mixture called fusel. Fusel is designated to be a mixture of higher alcohols containing more than 2 carbons, mostly isoamyl alcohol[6]. Fusel is produced in the bottom of bioethanol rectifying columns. Figure 1 details a typical bioethanol column.

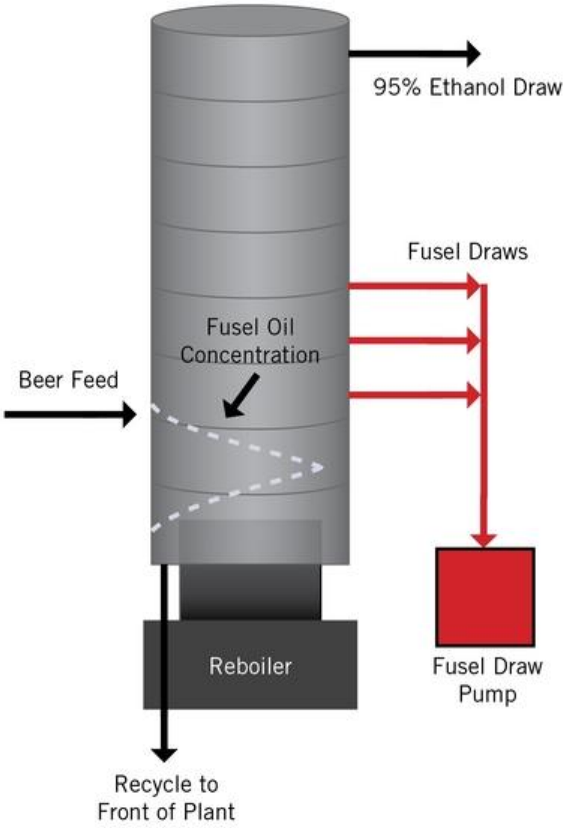


Figure 1: Bioethanol rectifying column

As seen in Figure 1, the bottom of the column is heated, driving the vapors up the shaft. As they move up the column the volatility of the higher alcohols decreases, and they recollect at the various points in the column.[7] The combination of these draws are known as fusel.

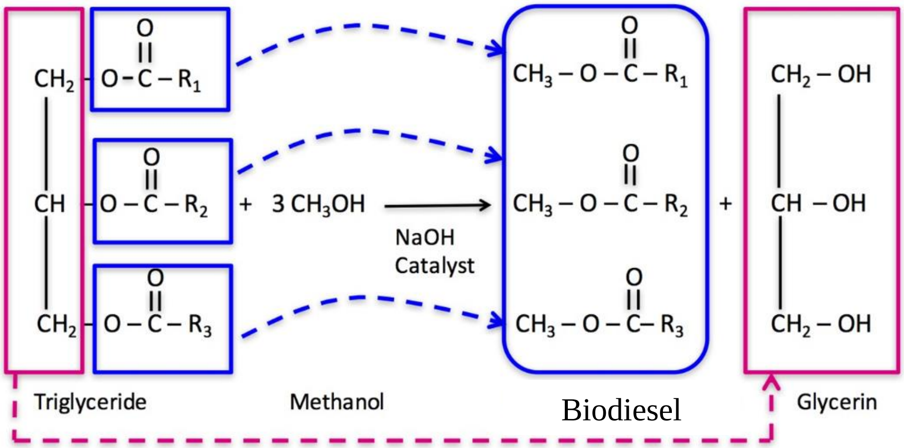
The combination alcohols varies by sample but on average fusel is about 15 percent water and 55 percent isoamyl alcohol[8]. Table 1 details the full composition of fusel. Isoamyl alcohol makes up most of the fusel composition with water being the next highest. It is possible to separate each of these alcohol components individually with different distillation techniques in the rectifying column.[9-22] However, this greatly increases the cost. The aim of this research is to use the raw fusel with minor treatments to create an effective fuel for charcoal briquettes.

Table 1: Average composition of fusel from bioethanol production

Compound	**Average composition**
isoamyl alcohol	55.70%
active amyl	12.07%
isobutanol	6.71%
butanol	0.57%
pentanol	0.94%
propanol	0.94%
ethanol	8.66%
methanol	0.02%
water	15.31%

The major challenge to using fusel directly as a fuel is its high water content. Awad *et al* show that lowering the moisture content in fusel from 15% to 6 % created a 13% improvement in heating value for fusel-gasoline blends in spark-ignition engines.[23] For this study, a combination of glycerin and biodiesel will be used to dehydrate the fusel to lower than 3 percent to promote enhanced heating values for fusel.

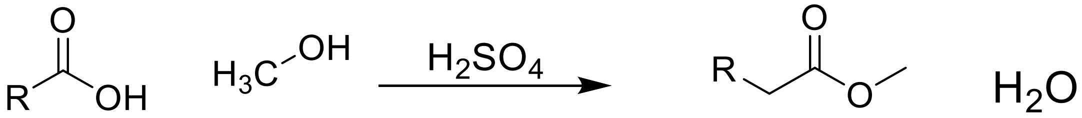
Scheme 1: Reaction of Triglycerides to make Biodiesel



Biodiesel was created as a fuel source to offset some petroleum usage. Vegetable oil was used originally, but its high viscosity rendered it unusable[24]. Since then various chemical medication have been used to lower the viscosity, the most common being transesterification. This transesterification reaction between triglycerides and methanol, or any other alcohol creates methyl esters which are collectively called biodiesel, scheme 1. In the United States, soy, corn, canola, and cotton seed oil are the primary sources for biodiesel production.[25] However other sources can be used such as feather meal, and used cooking oils to reduce the use of food products for fuel.[26] Since 2001 the production of biodiesel has been regulated under ASTM D 6751 which has metrics for viscosity, flash point and oxidation stability[27].

The transesterification of biodiesel can be catalyzed by either acid or base. Acid catalyst works well if the content on free fatty acid is high. Fatty acids come from the hydrolysis of triglycerides and with only esterify under acidic conditions to produce the methyl ester[28], see scheme 2.

Scheme 2: Acid catalyzed transesterification of fatty acids



Acid catalysts produce high yields of methyl esters but suffer from long reaction times, water sensitivity, high catalyst loadings of strong acids, like H_2SO_4, temperatures of over 100 C, and large excess of alcohol to drive the reaction.[29]

In the case of base catalyzed reactions, as seen in scheme 1, temperatures can be lower, as well as catalyst loadings as low as 1-2 mol%. They also require less excess of alcohol reagent though yields are slightly lower than with acid catalyzed. [30] In almost all cases, base is the preferred catalyst for biodiesel production.

During the production of biodiesel, the by-product glycerin is produced. Once the biodiesel reaction is complete and allowed to settle, the glycerin will phase separate and is easily removed. Estimates suggest that 1 kg of crude glycerin is generated for every 10 kg of biodiesel produced.[31] As such there is high interest in finding value for this waste product. However, it is not economically feasible for smaller plants to refine crude glycerin into pure glycerol.[32]

Table 2: Composition on various crude glycerin samples.

Samples	Soy-1	Soy-2	Soy-3	WV	SW
Free glycerol	63	22.9	33.3	27.8	57.1
Methanol	6.2	10.9	12.6	8.6	11.3
Water	28.7	18.2	6.5	4.1	1.0
Soap	BDL	26.2	26.1	20.5	31.4
Methyl Esters	BDL	21.3	19.3	28.8	0.5
glycerides	BDL	1.2	1.6	7.0	0.4
Free fatty acids	BDL	1.0	1.4	3.0	BDL
Ash	2.7	3.0	2.8	2.7	5.7
Total	99.4	102.9	101.8	101.1	103.6

BDL, below detection limit, WV, waste vegetable oil, SW, soybean oil and waste vegetable oil

As table two shows, crude glycerin can have as much as 28.7 percent water and as little as 22.9 percent pure glycerol.[33] While the vastly varying content of the different glycerin samples is discouraging for purification work, the high water content suggested crude glycerin would be a great dehydrating agent for fusel.

The process for the liquid formulation is two steps. Step 1 combines fusel and crude glycerin into a tank. The glycerin will phase separate and remove most of the water. Step two combines the treated fusel with biodiesel, driving out any remaining glycerin and water. This work seeks to optimize this process and apply it to instant light briquettes.

Instant Light Briquettes

When considering charcoal, there are two main types, lump charcoal and briquettes. Lump charcoal is more wood based and easier to ignite but does not have as long of cooking times as briquettes. Briquettes require more coverage to coat and longer to reach cooking temperatures but stay lit for much longer than lump charcoal. For instant light formulations, briquettes are soaked in lighter fluid then packaged.

The major standard regarding the lighting and emissions of charcoal briquettes is the South Coast Air Quality Management District (SCAQM) Rule 1174.[34] This is a California based test required before your product can be sold in state. It limits the VOCs that charcoal produces to 0.02 pounds per start. See Figure 2 for a model experimental setup. The standard details that for instant light briquettes 2 pounds of charcoal are taken and placed in stack with a diameter of 8.5 inches and a max height of 5 inches. The charcoal is required to be lit within 10 minutes of removal from its bag. The charcoal is ignited with an electronic probe or matches for a total of 12 trials over 3 days or less. There are also control burns of non-impregnated briquettes as a background sample, with VOC's limited to 0.008 ppm. The test is complete with the charcoal temperature reaches at least 200 F, VOCs are below 30 ppm for 2 minutes, the briquettes have undergone testing for 25 minutes, and the surface of the charcoal is covered in 70 percent ash.

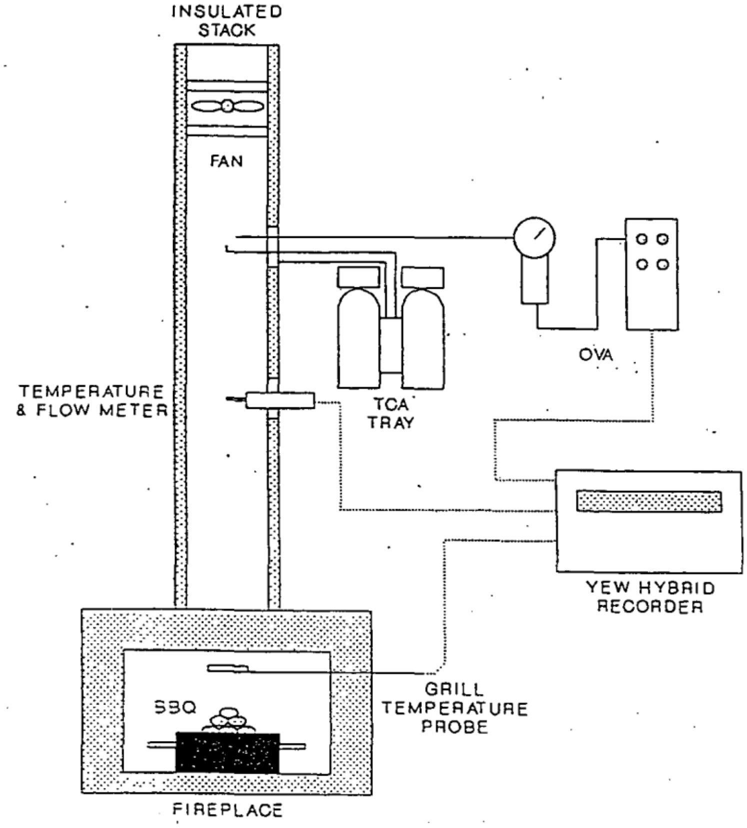


Figure 2: Testing apparatus for SCAQM Rule 1174 charcoal briquettes

For this study three types of briquettes were explored and are pictured in figure 3. The Buffalo briquettes are square, smooth and very dense. They are the largest briquettes of the three. The Naturals briquettes are smaller and have a curved shape with valley in the middle. The product claims the valley helps promote better air flow for flames. The last briquette type is a variation on the Naturals, called Embers. The Embers have the same curved shape but are impregnated with wood chips making them a hybrid between lump charcoal and briquettes. This work describes the loading and evaporation testing of all three briquettes to determine the optimal briquette for full scale burning tests.

Burn tests were performed at each stage of testing to ensure performance of the briquettes. Burning of charcoal can be divided into three distinct sections. There is the initial lighting phase. This is when the briquettes take a flame and the flame spreads to cover the entire briquette. For the purpose of this work, the flame had to last one minute to be considered successfully for initial lighting. The second phase is dubbed the ash phase. This is when after lighting, most of the briquette burns away leaving an outer coating of ash. For the SCAQM standard, 70% ash over is required to pass.[34] The third phase of charcoal burn, is flame extinguished. This is what charcoal manufactures advertise as this is when the charcoal is hot enough to begin cooking food. This is the most complete method of testing, but the longest. In the interest of processing samples quickly, this works used incremental increasing in the burn test phases with the initial briquettes only subjected to the initial phase, and the final large-scale trials undergoing a full burn test till flame extinguished.

Thesis Objectives

The objectives for this research was two-fold. The first objective was to optimize the liquid formulation of the lighter fluid. This included refining the procedure for the dehydration of fusel with glycerin and ensure this step preserved the high molecular alcohols needed for ignition. Along the dehydrating, the fusel needed to be treated to remove its distinct whiskey odor left over from the rectifying column. Once the fusel is treated, the second objective of this work is to impregnate charcoal briquettes with fusel to create a petroleum free instant light charcoal briquette. This work details briquette loading and evaporation tests as well as direct comparison to a major market competitor.

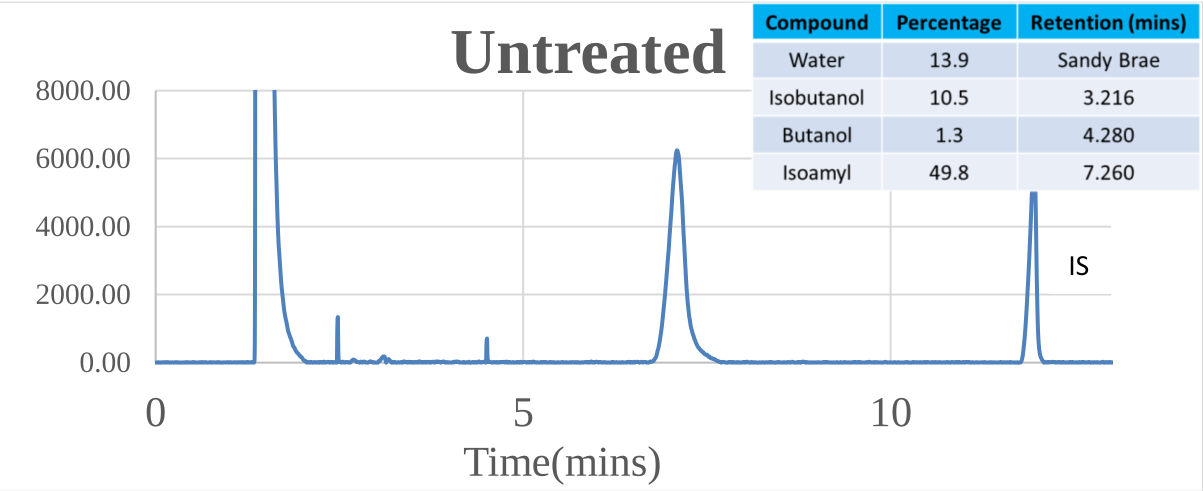
CHAPTER 2

OPTIMIZING LIGHTER FUILD FORMULATION

One of the objectives for this project was optimizing the processing of the fusel to remove water without reducing effective alcohol content. The previous formulations called for mixing fusel with glycerin and biodiesel to create a mixture that would spread well over charcoal. The glycerin and biodiesel additions allowed for water removal by phase separation. When this same formula was applied to instant light briquets, the volume of biodiesel was reducing the alcohol concentration so much so that it prevented ignition. The formula that worked effectively for lighter fluid would not work for instant light briquets. Since the second treatment with biodiesel could no longer be used to reduce the water content of fusel to below 3 percent, more exploration with the glycerin treatment was needed.

Glycerin Treatment

Raw fusel was treated with glycerin in varying percentages to observe the change in water content and any changes to alcohol content after treatment. To measure the water content in fusel, a sandy brae water test kit was used. It is most commonly used for oil and lubricants. The kit works by reacting the water in your sample with excess calcium hydride to produce carbon dioxide. The gas produced is then measured by a pressure gage which can then be converted to the amount of water present in your sample.[35] This method is quicker and easier to use than other methods of water determination like the Karl Fisher titrator. The sandy brae water test kits can measure up to 15 percent water content with testing time as short as 5 minutes. Gas chromatography (GC) was used to monitor alcohol content, specifically isoamyl alcohol, butanol, and isobutanol.



Compound	Percentage	Retention (mins)
Water	13.9	Sandy Brae
Isobutanol	10.5	3.216
Butanol	1.3	4.280
Isoamyl	49.8	7.260

Figure 3: GC and Sandy Brae results for raw fusel. Internal standard 5% anisole

The target for any treatment of the raw fusel was to reduce water content to below 3 percent without removing any of the isoamyl alcohol. Since the original lighter fluid formulation with fusel and biodiesel had a water content of less than 3 percent, that needed to be matched for the instant light formulation. The higher molecular weight alcohol would be needed for ignition and its low volatility would slow evaporation.[21]

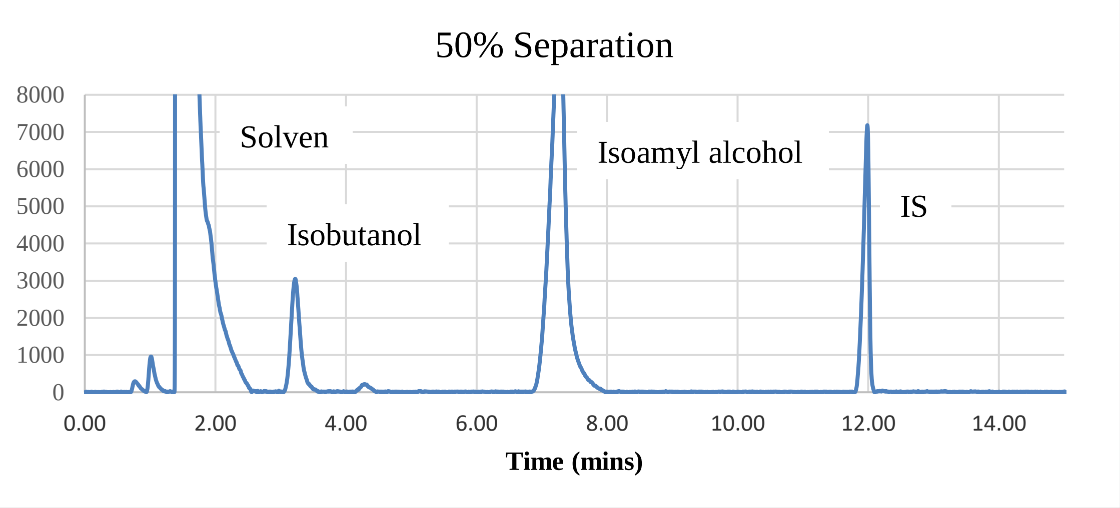


Figure 4: GC Results of 50% glycerin treated Fusel. Internal standard 5% anisole

The glycerin treatments ranged from 30% to 50% (v/v). Table 1 details the results of these treatments. After the treatments, the alcohol content of mixture increased, suggesting that while the treatment is removing water it is not removing the ignitable alcohols. The overall volume of the mixture was decreasing leading to an overall increase in alcohol content. The glycerin at 30 percent removes most of the water with diminishing returns as the percentage of glycerin increases. However, to reach the set metric of less than 3 percent water remaining, 50 percent (v/v) of glycerin needed to be used to treat the raw fusel.

Table 3: Complied GC results from treatment of raw fusel with glycerin

% Glycerin	**Isobutanol %**	**Butanol %**	**Isoamyl %**	**% Water**
50	**19.28**	**0.92**	**75.10**	**2.91**
45	**18.73**	**1.06**	**74.46**	**3.23**
40	**18.47**	**1.30**	**73.61**	**3.47**
35	**18.07**	**1.32**	**73.43**	**3.49**
30	**17.46**	**1.34**	**72.80**	**3.63**
Untreated	**10.52**	**1.37**	**49.82**	**13.92**

With these results, all further experiments were done on fusel that had been treated with 50% (v/v) glycerin to remove water.

Odor Treatments

The second objective for the treatment of fusel was to reduce its distinct odor. One possible source for this odor is butyric acid. Butyric acid is commonly found in rancid dairy products and in vomit. It is found in food to generate a sour taste.[36] It is produced during anaerobic fermentation and is more than 1000 ppm of fusel. Humans can easily detect was low as 20 ppm butyric acid.[37] Initial qualitative experiments where performed to find opium cost effective pathways before samples would be sent to an outside lab for butyric acid measurements.

The first attempts at odor removal involved the use of common odor removers such as activated carbon and using bases to hopefully neutralize the butyric acid with minimal addition of water to the mixture. 100ml of the glycerin treated fusel would be introduced to 5 grams of the odor remover for initial testing. The smell test was done on a purely quantality metric having first smelled the original fusel, then smell the odor treated samples and rank on a scale of improvement. The ratings were no reduction, mild reduction, moderate reduction, and significant reduction. The results of these odor treatments are detailed in table 4.

Table 4: Qualitative rankings for initial smell test

Treatment	**Smell Result**
Active Carbon	Significant Reduction
Silica	No reduction
Alumina	Mild reduction
Basic Alumina	Moderate reduction
Diatomaceous Earth	No reduction
Sodium Carbonate	No reduction

Since active carbon and basic alumina had the most promising initial results, further testing was done on mixtures of these two components to see if complete odor removal could be accomplished. The ranking this time was done on a 1-10 scale. Again 100 mL of fusel was subjected to each treatment. The results are detailed in table 5. The separations were designs to be as cost competitive as possible. Methods of column filtration were comparted to vacuum filtration and gravity filtrations to mitigate the cost of the odor treatment process.

Table 5: Smell study with active carbon and basic alumina

Separation Process	**Smell Ranking**
2:1 basic alumina: active carbon column 4in by 2in – 1st fraction-clear	1
2:1 basic alumina: active carbon column 4in by 2in — 2nd fraction-yellow	2
0.2g/ml active carbon, 1min stir, vacuum filtered	3
0.15g/ml Active carbon, 1min stir, vacuum filtered	4
0.15g/ml Active carbon, then 0.3g/ml basic alumina and vacuum filtered	5
0.15g/ml Active carbon, ran through a 2in by 2in column of basic alumina	5
0.15g/ml Active carbon, ran through a 5in by 2in column of basic alumina	5
0.1g/ml active carbon funnel filtered	6
Basic Alumina Column, 1/8in active carbon on top	7
Basic Alumina Column 5in, 2in circumference	8

From the results seen in Table 5, active carbon had the strongest effect on odor removal. There was a clear dependence on concentration observed as well. 0.15g/ml active carbon per fusel had a noticeable stronger smell than 0.2g/ml active carbon per fusel. This was also very evident in the two mixture columns of carbon and basic alumina. The first fraction, about 40mL of the column was clear and completely removed all odors. The second fraction became yellower and the odor increased though no to the level of any of the other trials. Moving forward, only active carbon was used as it had the strongest effective on odor removal and was less expensive than basic alumina.

Seeing the effective of the active carbon, cost analysis needed to be conducted to see if this treatment would be appropriate for the lighter fluid product. The target price for treatment was less than 30 cent per gallon to remain competitive in the market.

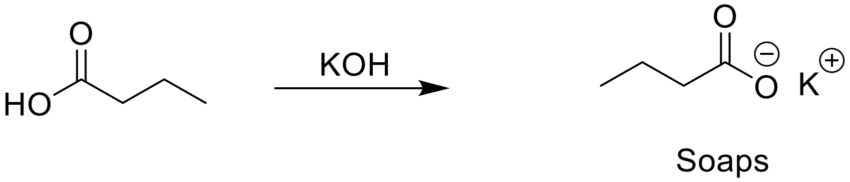
Table 6: Cost analysis for active carbon treatment

Percent Yield	**$/gal**	**Smell Remaining (%)**
87	4.24	0
91	2.02	15
91	1.59	40
91	0.83	45
93	0.40	80
93	0.27	85

Table 6 above shows the results of the cost analysis study. The original treatment where all the fusel is clear and has no odor would cost over 4 dollar per gallon just for the additional treatment. There was also a slight yield loss with each treatment that was not considered in the cost analysis. The later trials were run in ranges that would be cost competitive. However, the effective odor removal previously seen was lost. The raw fusel has so many contaminants that it is saturating the active carbon above concentrations that are cost effective.

The next treatment sought to chemically modify the fusel through alkaline transesterification of the butyric acid. Base catalyzed transesterification is the same process used to make biodiesel, so the materials would already be on site. Biodiesel is the transesterification of fatty acids or triglycerides into alkyl esters using alcohol typically methanol. The reaction can be catalyzed by acid or base. Typically for biodiesel if the free fatty acid content is high, acid catalyst is used.[38, 39] However, since fusel is less than 1 percent butyric acid, base was used. There was a concern with the health risks of burning excess acid and using base requires lower temperatures, lower catalyst loading and less time. Typical base catalyst loadings range from 1-5 mol %.[40] The base catalyst would also heterogenous so easily removed after treatment.

Scheme 3: Transesterification of Butyric acid



Scheme 3 details the reaction, where carboxylic acids present in the fusel could react with the butyric acid, forming soaps.[24] In biodiesel production, soap formation reduces the yield of methyl esters. However, since soaps phase separate from fusel and are very soluble in glycerin, they can be removed with the glycerin treatment discussed previously with no losses to alcohol content.

The transesterification was created to vary temperature between 22 and 40 C. While the ideal temperature for this reaction is around 65 C[41], the flash point for fusel is 60 C[23], so all temperatures need to below that point. Potassium hydroxide catalyst was varied from 0.5 wt % to 5 wt % and time went from 1 hour to 18 hours. To fully quantify these chemical changes all samples were sent for butyric acid analysis. The summarized results of the transesterification are presented in Table 7.

Table 7: Summary of Butyric acid content after transesterification

Sample	Temp	Time	KOH wt%	Butyric Acid (ppm)	Yield %
Control	0	0	0	1234.2	100
1	22	1	0.5	818.7	91.98
2	22	1	5	665.5	83.21
3	22	9.5	2.75	537.3	82.77
4	22	18	0.5	606.7	88.18
5	22	18	5	604.8	82.41
6	40	9.5	0.5	584.5	92.82
7	40	9.5	2.75	504.6	81.41
8	40	9.5	5	281	82.41

The original fusel sample starts out at 1234.2 ppm of butyric acid. Starting at ambient conditions and increasing time and catalyst loading, there appears to be a balance in time where the reverse reaction hydrolyzing the ester begins to dominate after 9.5 hours. Moving forward with slight heating, the optimum result was 40C with 5wt % catalyst for 9.5 hours. There was observable excess catalyst in the flask indicating the solution was saturated and an increase in catalyst loading would not be effective. The water byproduct and excess base could then be removed with the glycerin treatment discussed above. While the butyric acid content is still above the human limit of detection[37] this treatment created a more than 4 fold reduction. Plans are currently in place to implement this process into the current production methods.

CHAPER 3

INSTANT LIGHT BRIQUETTES

After the optimization of the lighter fluid formulation, the next step was to create an instant light briquet product. Several factor would need to be tested. First the briquette would need to be chosen based on level of fusel absorption. Then evaporation tests would be conducted to determine the maximum time before bagging. Once the briquette formulation was optimized, burn tests could be conducted for single and multiple use bags.

Briquette Selection

Three briquettes were sourced for these tests. Buffalo, Embers, Naturals. Buffalo briquettes were the densest of the three and made primarily from corn starch. Naturals were the smallest briquettes and molded into a curved shape. Embers had the same shape as Naturals but included small wood chips in the formulation.

Figure 5: Charcoal Briquettes, Left to Right Naturals, Embers, Buffalo

Loading tests were done in 10 second intervals and allowed to dry for 3 mins before mass measurements were taken. As seen in table 8, the buffalo briquettes required more than a 40 second soak time to ignite, with a fusel loading over 4 grams per briquette. Naturals had successful lighting even after 10 seconds but had a fusel loading of less than 4 grams. Embers saw a similar trend to Naturals but with much more variation between samples. The wood chips created cracked or broken briquettes. It was these cracks that allowed more fusel to impregnate the briquet, surpassing the buffalo briquets with only a 10 second loading time.

Table 8: Fusel Loading Test, 3 Briquette types

Briquette	Dip Time (sec)	Average Loading	Burn (y/n)
Buffalo	60	4.313g	Y
	50	4.102g	Y
	40	3.729g	Y (slow)
	30	3.394g	N
Naturals	60	3.879g	Y
	50	3.728g	Y
	40	3.302g	Y
	30	2.776g	Y
	20	2.437g	Y
	10	2.225g	Y
Embers	60	3.879g	Y
	50	3.728g	Y
	40	3.302g	Y
	30	2.776g	Y
	20	2.437g	Y
	10	2.225g	Y

Figure 6 details the linear comparison between all three briquettes and their soak times which can be used to calculate cost with varying soak times once the briquets are in production. It is also very evident that the Embers briquettes have an extremely high loading of fusel compared to the other two. Due to this and the high number of broken briquettes per bag, Embers was excluded from the evaporation studies.

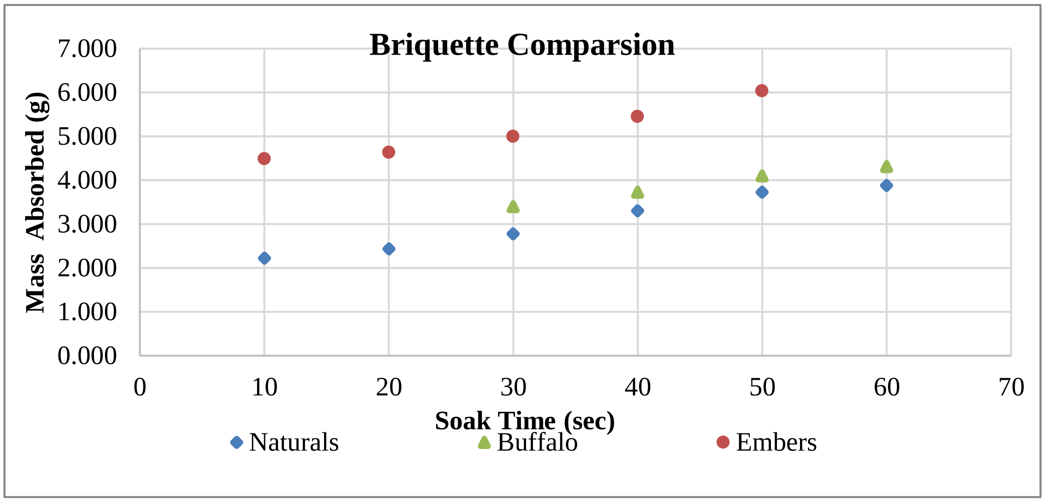


Figure 6: 3 Briquette type Comparison

For the evaporation tests, both briquettes were soaked for 60 seconds to allow for maximum fusel loading. After 3 mins the briquettes were dry to the touch and the evaporation tests could start. The overall evaporation loss for both briquettes over 30 mins, Figure 7 a. After 30 mins the percent fusel lost is about the same. However, Figure 7b shows an excerpt of the graph from times under 10 mins. This is the most probable time for bagging to take place. In the shorter time frame the denser buffalo briquette has a slower evaporation rate. The is probably due to the fusel penetrating deeper into the briquette allowing delayed evaporation. Looking back to Figure 7a we can see that the evaporation rates are about equal at 15 mins, then the Buffalo briquettes experience a small spike in rate, possibly an effect of the evaporation delay bring more fusel to the surface, before the rate evens out with the Naturals briquettes.

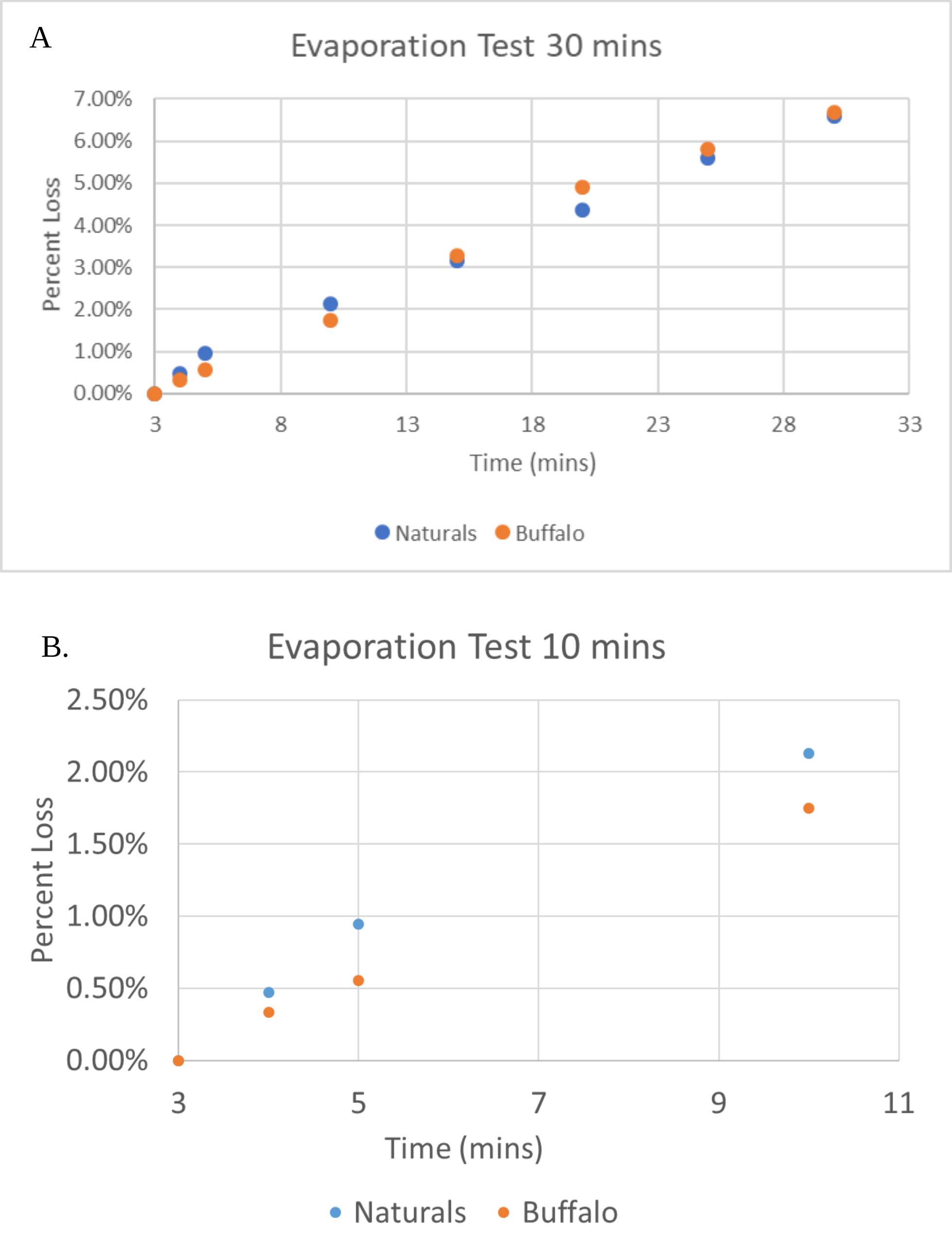


Figure 7: Evaporation Tests Buffalo and Naturals. (A over 30 min, B over 10 mins)

Due to the slower evaporation rate at short time scales, Buffalo briquettes were selected for further testing with the bag time limited to under 5 minutes.

Coatings

To slow the evaporation rate further, a coating was to be applied to the briquettes. The desire was for the coating to seal the briquette and then melt during lighting to allow ignition of the briquettes. Olein palm oil had some success in this endeavor. Palm oil is an edible oil made from the fruit of palms. In the year 2016, palm oil contributed up to 30% of oils and fats production globally[42]. It differs from other vegetable oils in its high concentration of saturated fatty acids[43] . Palm oil is fractionated during production and the semi-solid olein fraction was used here. Its low melting point and smooth coating properties made it perfect for coating briquettes[44, 45].

The main goal of the coating was to extend the time the briquette could be exposed to open air before failing to ignite. To test this, the briquettes would be loaded with fusel dipped again into a coating mixture for a 2-step process. After being exposed to air for varying times, the briquettes would be lit, and time recorded until ash was seen. Ash presence indicates burning of the briquette after the ignition phase. This would be before the charcoal is ready to be used in cooking but is an indication of full ignition of the briquette without the flame going out.

Table 9: Summary of the coating mixtures and burn time results

Coating	1-hour Dry; Ash time	4-hour Dry; Ash time
No coating	4:12	No burn
Palm Oil	No burn	-
50:50 Palm Oil Fusel	4:58	5:15
75:25 Palm Oil Fusel	4:54	No burn
90:10 Palm Oil Fusel	5:32	No burn

As seen in Table 9, a mixture of palm oil and fusel had to be used for the coating. Pure palm oil sealed the briquette, preventing access to any volatiles for ignition. The 50:50 mixture of palm oil to fusel proved to be the best at slowing evaporation rates. This ratio was the best mixture for providing fusel at the surface to ignite and sealing the fusel loaded in the briquette.

However, this coating would not allow for the briquettes to be placed in traditional paper bags used to store charcoal. The coating requires some fusel to be present in the top layer to promote ignition. With transportation, this would no longer be the case once the product reached the customer. In addition, it would be quite costly to add a second dip as the current plants only have equipment designed for one dip processes. Instead, to prevent evaporation the briquettes will be bagged in bio sourced packaging that can be heat sealed.

Market Comparison

With the formulation and the bag design complete, it was appropriate to test the new briquettes with the fusel fuel against the major name brand petroleum competitor. In order to have a place in the market, the new briquettes would have to be competitive in performance quality with what is already on the market. The first test study would be in the context of a single use bag. This was an important consideration as the bio-based formulation does evaporate, and while that evaporation is controlled for in bagging, it was important to verify how long the bagged product could be open before the effectiveness of the briquettes was reduced.

For the single use burn test, briquettes were loaded with fusel for 60 seconds and then left in atmosphere for varying lengths of time. The competitors instant light briquettes were also exposed to the same drying conditions. Small samples where then taken and burned, with burn time being recorded after the flames had extinguished. This measurement instead of ash over was chosen to ensure consistence and to compare to the advertised extinguish time of the competitor, 10 minutes.

Table 10: Single Use bag Burn Test Results

Briquette	Burn Time	Dry Time	% Fusel Loaded
Fusel	7:30	30 mins	13.25
	7:15	1hr	12.19
	6:45	2hrs	11.25
	None	4hrs	14.45
	None	18 hrs	13.09
Competitor	9:30	2hrs	
	11:34	4 hrs	
	6:37 (weak)	18 hrs	

As shown in Table 10, the fusel briquettes burned well in the shorter time scales. The burn times were even shorter than those advertised by the competitor. This means that the fusel briquettes would be at cooking temperature faster than the competitor briquettes. However, at longer timeframes, the fusel briquettes begin to fail. At 2 hours, the burn time was shortened by 30 seconds. At 4 hours the briquettes failed to ignite at all. The competitor briquettes burned well at 2 and 4 hours but after 18 hours had a weak flame that extinguished prematurely.

In the context of a single use bag, while the fusel loaded buffalo briquettes did not perform as well as the competitor briquettes in the longer time scales, they did perform well in time scales less than 2 hours. A customer could open the bag of fusel briquettes and leave it open for 1 hour and the briquettes would still perform well. This was considered a very reasonable time frame and the product was moved forward for production with a single use 3lb bag of instant light briquettes.

Multiple Use Bag

After verifying the feasibility of a single use bag, the next step was a multiple use bag. This bag would have to be totally sealable to prevent the evaporation of the fusel. The main challenge was with multiple openings and closings would the briquettes still light if the total exposed time was limited to 60 minutes. To mimic the production process, briquettes were soaking in fusel for 60 seconds then dried and sealed in five minutes. As there was no proto-type bag as the time of these experiments, a sealable polypropylene container was used. Before going to market, a bio-based bag would need to be developed and tested, but this experiment can serve as a model.

Table 11: Multiple Use bag Burn Test Results

Briquette	Burn Time	Total Dry Time	Total Days
Fusel	-	15mins	0
	7:15	30mins	1
	7:25	45mins	2
	7:02	60 mins	3
Competitor	-	15mins	0
	8:43	30mins	1
	8:42	45mins	2
	none	60mins	3

As Table 11 shows, the fusel briquettes are still lighting well after being in the sealed container for 3 days and opened 4 times. The burn times stayed around 7 minutes, the same as the single use bag. This very clear demonstrates that a multiple use bag is possible for these briquettes. Total exposed time was kept at 60 minutes, given what was seen in the single use bag test. However, it may be possible to increase soak time if the bag needed to be stretched for more uses.

In the case of the competitor, we saw shorter burn times than in the of the single use bag tests. There was also observable deformation to the container, likely due to the petroleum volatiles penetrating the container. The loss of the ignitable volatiles leads to the competitor briquettes failing at the 3-day test.

Figure 8: Day 3 Burn Test, Right Fusel, Left Competitor

Figure 8 shows the briquettes after the day 3 burn test. The fusel briquettes have a much larger ash content and show a more complete burn than the other briquettes which only have ash around the edges.

These initial experiments show great promise for the future introduction of a multiple use resealable bag to the product line. Further testing would need to be done to test the longevity of the multiple use bag and see if the exposed time could be lengthen allowing for larger bags. They would also need to be tested with the final bio-based bag to ensure there was no penetration of the violates into the packaging and the resealed seal would hold over the duration of the test.

CHAPTER 4

CONCULSION

The overall goal of this project was to improve the formulation of the current fusel based lighter fluid and use it to create an instant light briquette product that could be brought to market. The improvements that needed to be made to the liquid formulation included water removal and odor treatments.

For the liquid formulation, glycerin was used as a dehydrating agent and was tested a various percentage to achieve below 3 % water content in the fusel. It was found the a 50:50 ratio of glycerin to fusel achieved this metric while preserving the high molar weight alcohols that that give the lighter fluid its ignition properties. For the odor treatment various methods were attempted. Treatment of fusel with large amounts of activated carbon did successfully remove all odor and color from the product but the large amount of active carbon needed made the treatment not cost effective. The base catalyzed esterification of butyric acid, the same process to make the biodiesel used in the liquid formulation, was found to create a fourfold reduction in butyric acid content when compared to an untreated sample. However this reduction still has the butyric acid content higher than the human limit of detection[37] so more work needs to be done in this area.

To design the instant light briquette product several factors needed to be explored. First the briquette type needed to be chosen with respect to soak time and evaporation prior to bagging. It was found that a 60 second soak time and a bag time of under five minutes was ideal for this product. The thickness of the briquette meant that more fusel could be loaded to the briquette and that initial evaporation rate was slower, leaving longer times for bagging.

The second factor that was explored was bagging and a direct comparison to competitor briquettes. First, single use bags were explored. It was found that the fusel loaded briquettes had shorter flame times compared to the competitor but could only be exposed to atmosphere conditions for 1 hour before they began to lose performance characteristics while the competitor took 18 to see similar failure. However, for a single use bag, 1-hour exposure is reasonably within the time of use for the costumer. The single bag product is currently being brought to market.

For the multiple use bag, the fusel product was compared to competitor briquettes over the course of 3 days stored in resealable polypropylene containers. It was seen that if the total exposure time was limited to 1 hour, the fusel briquettes performed well over the 3-day period. The competitor briquettes had volatiles being absorbed by the container, and experienced failure on the third day. This is strong supporting evidence for the feasibility of large multiple use bags for the fusel briquettes.

The results of this study led to a totally new product being brought to market with the single use bag of fusel briquettes. More work still needs to be done on odor treatment but the 4-fold reduction with esterification is a good start. Multiple use bags are another area of future work in testing times longer than 1 hour and testing the resealable nature of the bag that would be created for this product. Overall, this research work was successful in its goal of creating a bio-based instant light briquette that can be competitive in the market.

CHAPTER 5

EXPERIMENTAL DETAILS

Materials:

Glycerin and Fusel and all charcoal briquettes were provided by ESCOGO. Palm oil was purchased from Jedwards International. All other materials were purchased from Sigma Aldridge and used as received. Production of all final materials was done at the ESCOGO plant in Monroe GA

Water analysis:

A water test kit was purchased from Sandy Brae Laboratories. The kit can test for water content ranging from 0.005% to 12% water in various liquid medias. To test for water excess calcium hydride is added to the pressure vessel. The sample liquid is then mixed with the calcium hydride to produce hydrogen gas. The reading on the pressure vessel can then be converted to water content in the sample. This was done for all samples pre and post glycerin treatment.

Gas Chromatography:

A gas chromatograph SRI 310C was used during these experiments. The column oven was set at 250 C. Chromatographic separation was achieved using a Restek MXT capillary column (15m × 0.53 mm I.D., 5 μm) with the following temperature program: 40 C, held for 5 mins, then ramp at 10 C per minute to 200 C then held for 5 minutes. The sample injection volume was 1μL and helium was used as the carrier gas at a 1.0 mL/min flow rate. Anisole was used as an internal standard at 5%.

Procedures:

Glycerin Treatment

Raw fusel was added to a separatory funnel with varying ratios of glycerin. Solutions were mixed then allowed to settle for 24 hours. Glycerin layer was removed. For instant light formulation, fusel was used without further treatment. For lighter fluid formulation, biodiesel was added, and a second water layer was removed prior to use. All fusel used in further experiments apart from the esterification was done with fusel that than undergone this treatment.

Odor treatment

The broad screening as described in table 2 was a mixture of 100 mL of fusel oil with 10 grams of either active carbon, silica, alumina, basic alumina, diatomaceous earth. All mixtures were then stirred for 1 hour then vacuum filtered, and smell changes recorded. For the sodium carbonate sample, carbonate was added in excess and stirred with fusel overnight. Remaining carbonate was filtered, and smell changes recorded.

The secondary screening with active carbon and basic alumina was performed with 100mL of fusel being exposed to the treatments described in table 3. The resulting eluent was then ranked in order of qualitive smell.

The cost analysis of the activated carbon is based on a quote of $3.41 per kilogram. Samples were filtered through a 4in by 2in column of active carbon in varying volumes to reflect varying price points. Percent yield was calculated based off the amount of eluent collected and smell removed was estimated based on direct comparison to before and after samples.

Esterification of Butyric Acid

100mL of fusel was combined in a flask with potassium hydroxide in various catalyst loadings and a magnetic stir bar and sealed. Using varying temperatures and times the esterification was conducted. (see table 7) The mixture was then allowed to settle in a separatory funnel overnight. The soaps later could then be removed, and the treated fusel sent for butyric acid testing.

Briquette Loading

For each of the three briquette types, Buffalo, Naturals, and Embers, 3 briquettes were placed in a bath of fusel and allowed to soak. After the designated soak time, the briquettes were left to dry on wire racks for 5 minutes. Mass was taken before and after to get amount of fusel loaded. The briquettes were then stacked in a house of cards fashion and lit. A sustained flame for more than 1 minute was considered a successful light.

Briquette evaporation

For each of the briquette types, Buffalo, and Naturals, 3 briquettes were placed in a bath of fusel and allowed to soak for 60 seconds and dry on wire racks for 3 minutes. Mass loss was recorded once a minute for 5 minutes, then once every five minutes for 30 minutes.

Palm oil coatings

Three buffalo briquettes were soaked in fusel for 60 seconds and allowed to dry on wire racks for 5 minutes. Then the briquettes would be dipped into the coating solution and removed in less than 5 seconds and allowed to dry for either 1 or 4 hours. The three briquettes would again be stacked in a house of cards pattern for ignition. Burn time was recorded from ignition to initial ash.

Single Bag Burn Test

Buffalo briquettes were soaked in fusel for 60 seconds and allowed to dry on wire racks for 5 minutes. Buffalo and competitor briquettes were then left in ambient conditions for up to 18 hours. Burn test were performed at varying time points in a house of cards pattern. Burn time was recorded from ignition until flames extinguished.

Multiple Bag Burn Test

Buffalo briquettes were soaked in fusel for 60 seconds and allowed to dry on wire racks for 5 minutes. The briquettes were then bagged in polypropylene containers as were a sample of competitor briquettes. The containers were left open for 15 minutes then sealed overnight. This process was repeated for 4 days with burn tests starting on the second day. A total of 10 briquettes were removed for each burn test and time was recorded from ignition till flame extinguished.

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