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Abhijith Madabhushi

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Development of biomass-based form coke production process

By

Abhijith Madabhushi

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Development of biomass-based form coke production process

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Metallurgical coke is an important component of the iron and steel industry. It is obtained from high quality coking coals like bituminous coal. However, due to the limited resources and high levels of Green house Gases, alternatives to the product are of high demand. Availability of raw materials is an important factor. The product should have high heating value, strength and lower emissions. Research is being done on form coke technology; to produce high quality substitutes with inexpensive materials like lignite. A biomass-based form coke production process is developed. Two types of raw materials are selected at beginning of process. However, an ideal choice of raw material is evaluated by comparing the quality of the specimens produced from each substance. Various stages of the process are developed and their operating conditions are evaluated. The specimens developed are sent to a test facility to test reactivity and strength after the reaction.

DEDICATION

I dedicate this work to my parents, sister and my friends.

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I express my gratitude towards my advisor Dr. Richard Patton for his immense support and advice during the course of this work. This work would not have been possible without Mr. Neal Glasgow and Mr. Ken Moss, who provided the raw materials required for our research. I thank Dr. E. William Jones and Dr. Steven R. Daniewicz for serving on my committee. I am grateful to Mr. Vic Latham of Patterson Engineering Laboratories for helping me with the development of the compression mold required for the research. I also express my gratitude towards the Personnel of the testing facility at ArcelorMittal, who were gracious enough to conduct the testing required to validate our efforts.

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CHAPTER I

INTRODUCTION

Coke is a product of coal and is extensively used in many metallurgical applications. One of the most important functions of coke is as a heat source and a reducing agent in the smelting process of iron ore in a blast furnace, resulting in the production of pig iron. Obtained usually as a product of destructive distillation of bituminous coal, it is low in ash content and sulfur. This form of coke is also known as metallurgical coke. It is grey, hard and porous. Other forms of coke can be produced from man-made efforts. Interestingly, these are the cokes which are most commonly used, due to the fact that products with desired physical and chemical properties aimed at a specific purpose can be produced.

Coke is the more preferred fuel instead of coal in many industrial applications since it has more than 95% Carbon, the rest being ash. The absence of volatiles results in the effective combustion/utilization, lower probability of slag formation and less smoke.

1.1 Pet Coke

Petroleum coke or more commonly pet-coke, can be obtained as a carbonaceous solid residue from oil refinery coker units. More prominently, it can be produced from the cracking process; which is a delayed coking process in which the crude charge is mixed with the coker gas oils and fed to the heater. The cracking process then occurs inside the

heater resulting in the conversion of the charge into vapor and liquid. This efflux of vapor and liquid from the heater then flows into a container called the coke drum where the liquid drops out and is solidified [1]. While pet-coke is not as valuable as other high value petroleum products, it is available in different forms like catalyst grade, marketable fuel grade and marketable calcined pet-coke. While catalyst grade pet-coke is used as a fuel in the petroleum refining process, marketable fuel grade pet-coke is used as a substitute for coal in cement plants and power plants. Calcined pet-coke is used to make electrical components due to the fact that it has the highest carbon content and is the most pure [2].

1.2 Need for alternatives to metallurgical coke

Greenhouse Gases (GHG) are a cause for grave concern from an environmental standpoint and the iron and steel industry, is a heavy emitter of these gases. Data provided by the World Iron and Steel association proclaims that an average of 6.5% of global emissions of these gases is due to the production of ferrous materials [3]. The usage of metallurgical coke in these processes alludes to this fact. Also, the fossil fuel sources (coal included) are exhaustible and are depleting rapidly due to the increasing rate of consumption. Studies point to an experimental technique in which the CO₂ from the fuel can be captured and sent to safe storage areas without being exposed to the atmosphere. However, the technology has not been validated practically.

Consequently, a market has emerged for alternatives to metallurgical coke which can replace it at a commercial level. But, the product in contention should use resources other than high quality coking coals while having characteristics like a *high calorific value*, the ability to release *lower greenhouse gases* and finally, higher strength than coal.

The form coke process presents a viable alternative to the conventional metallurgical coke, thus replacing it in at some capacity in steel industry.

1.3 The Form coke process

The form coke process is executed in a series of steps starting from the pre-process treatments of raw materials to the briquetting and subsequent carbonization. At a broader level, any coke obtained from non-coking coals and a binder as raw materials is known as form coke and the process is known as the formed coke process. It involves the briquetting of char, biomass, coke and/or raw coals as the feedstock [4]. The usage of a binder material permits the use of a wider range of coals as feedstock and helps in securing a more consistent product quality. It also allows for the specimen to be shaped, followed by subsequent carbonization [5]. This technology attempts to produce a fuel that has properties analogous to those of metallurgical coke, or in some cases more beneficial, since form coke can be controlled and reproducible; it can be run continuously or periodically with a better control on pollution [6].

The foundation for the modern process was the clean coke initiative undertaken by U.S. Steel in the 1950s and the 1960s under contract with the U.S. Government (*Energy Research and Development Administration*), which aimed at producing cleaner metallurgical coke from de-sulfurized char and heavy residual oils from the process. The production process concentrated on making agglomerated coke specimens (briquettes and or pellets). Since the raw materials of this process were procured from a single source as stated above, there was potential for producing a superior product at the most reasonable cost [7].

Therefore, the form coke process produces a viable alternative option to the conventional metallurgical coke, producing coke with desired properties intended for specific purposes. Although the idea is attractive, there are quite a few challenges which have to be overcome in order to replace conventional coke. Proximity of the raw material sources, quality of the form coke produced (composition, impurities), high initial setup costs, time and money spent on research and development of form coke pilot plants are some of the issues which have to be dealt with. Even though the form coke domain faces the above challenges, the need for an inexhaustible and environmentally friendly coke prompts and encourages research.

1.4 Biocoke as an alternative

In a bid to fulfill the regulations and restrictions imposed by the authorities, research is being done in an effort to produce biocoke i.e., coke obtained from biological sources. Haque et al. [8] performed a study on the performance of biocoke-based carbon anodes in aluminum reduction cells for the production of aluminum. In the study, the biomass based anodes were prepared using a CSIRO patented technology of making biocoke. The process can be described as a high temperature pyrolysis process of wood under mechanical compressive force. They evaluated the total non-renewable GHG emission of Bio-coke production. It was 50 to 155 kg CO₂, which is much less than the GHG footprint of the anode grade petroleum coke (402 kg CO₂).

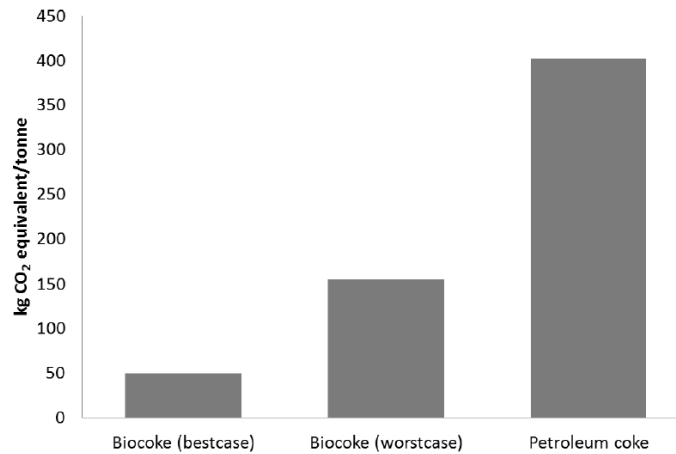


Figure 1.1 GHG footprint of bio-coke and petroleum coke production

1.5 Exploring charcoal as an alternative

Steel industries outside of the US, *viz.* the Brazilian steel industry employs charcoal in its blast furnaces. Since it is produced from wood, charcoal does not have sulfur (S) in its chemical composition and also has very low ash content. This allows for its usage in the blast furnace to produce better quality pig iron and steel. Owing to this fact, the Brazilian steel industry generates US\$ 2.0 billion per year from 60 % of the 10 million tons of pig iron, produced using charcoal [9].

However, there are certain disadvantages of using charcoal in the blast furnace. From Table 1.1, the percentage of fixed carbon content in charcoal is between 65-75 %, whereas coke tends to have more than 95% carbon, as mentioned earlier. Also, charcoal is produced at an operating temperature of 300 to 400°C and hence there is potential for more volatiles to be present in it. The compressive strength of coke tends to be higher than that of charcoal.

Consequently, the heating value and the energy density of charcoal is lower than coke. The major disadvantage of using coke in the blast furnace is the sulfur oxide (SO_x) formation and the higher ash content. The advent of the form coke technology and the research being done in biocoke domain may mitigate the situation in the favor of coke. Another disadvantage in using charcoal is its low heating value and energy density. The heating value of charcoal is about 28-32 MJ/kg whereas the heating value for a medium volatile coke can range up to 37 MJ/Kg. Because of lower heating value and lower compressive strength, a charcoal blast furnace is smaller in size compared to a coke blast furnace.

Due to the reasons specified above, it can be observed that the production capacity of charcoal based blast furnaces is less than its coke counterparts. In summary, formcoke/biocoke with low sulfur and ash is more viable and productive to use in blast furnaces in the United States when compared to charcoal.

Table 1.1 Comparison of properties of charcoal and coke

S.No	Parameter	Charcoal	Coke
1	Fixed Carbon	65-75%	> 95%
2	Ash content	2-5 %	10-12 %
3	Volatiles	25-35%	< 1%
4	Sulfur	0.03-.10%	0.45-0.70%
5	Compression Strength kg/cm ²	10-80	130-160
6	Heating value MJ/Kg	28-32	37

1.6 Overview

From the above discussion, it is apparent that coke is an important raw material necessary for the reduction of iron ore to iron; which is changed to steel [10]. However, the problems of ineffectiveness and obsolescence of the in-house coking ovens and the continuous need to adhere to the environmental standards warrant research in the form coke domain to provide more eco-friendly metallurgical coke alternatives which can be produced from sources other than fossil fuels.

In the following section, an in depth discussion on the factors affecting the form coke process is provided.

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CHAPTER II

FORM COKE TECHNOLOGY

The formed coke process involves the briquetting of char, biomass and non-coking coals as the raw materials. The usage of a binder material permits the use of a wider range of coals as feedstock and helps in securing a more consistent product quality. This technology attempts to produce a fuel that has properties analogous to those of conventional coke. The usage of the binder in some coke making processes allows for the coal to be shaped, followed by subsequent carbonization [1]. The major requirement for form coke (in addition to a high calorific value and constant carbon content) is the ability to retain its shape and form during exposure to heat in a furnace [2].

2.1 Literature Review on the Form coke Process

The process constitutes a series of steps ranging from material processing, feeding, calcination/shaping, carbonization followed by subsequent cooling. Investigation of the form coke process has been done by many eminent researchers. Holowaty et al. [3] initially developed a process of making formed coke from high sulfur coal containing 1.5 to 4 percent by weight sulfur to obtain char and formed coke product having 0.8 or less sulfur percent by weight.

Jauro et al. [4], in a bid to help Nigeria utilize its large deposits of iron ore, designed a method to manufacture coke from the formed coke process after investigating

the suitability of Nigeria's three major non-coking coal varieties which are Onyeama, Lafia-Obi and Garin Maiganga. It was found that the Onyeama and the Lafia-Obi coals or their blends could be the feasible alternative raw materials for the coke production. Since there is a serious shortage of coking coals in Nigeria, the formed coke process could be an attractive prospect.

A lot of the initial efforts were directed on producing coke from low quality non-coking coals under a number of different conditions. It aimed at developing the technology to produce solid formed cokes of high mechanical and chemical strength from low rank coal. Shimohara et al. [5] from the research laboratories of the Nippon Steel Corporation conducted a study to examine the factors influencing the strength of formed coke created from co-preheated coals. The co-preheat treatment of coals involved crushing and mixing the coals with the additive at a given mixing ratio and varying heating rates. The coke thus produced had CO₂ reactivity close to metallurgical coke at 1000°C.

Another process conceived as a response to the "Clean Air Act" was the preparation of Form coke from the "Continuous Carbonite Process" [6]. An ambitious project, the operation intended to produce high quality coke from both coking and non-coking coals with less operating cost in an environmentally friendly manner. The method of coke production through this process can be defined as a two stage continuous carbonization process in which char/Carbonite is first produced at 550°C. The Carbonite is then blended with the binder and briquetted and then subjected to further carbonization at 1200°C.

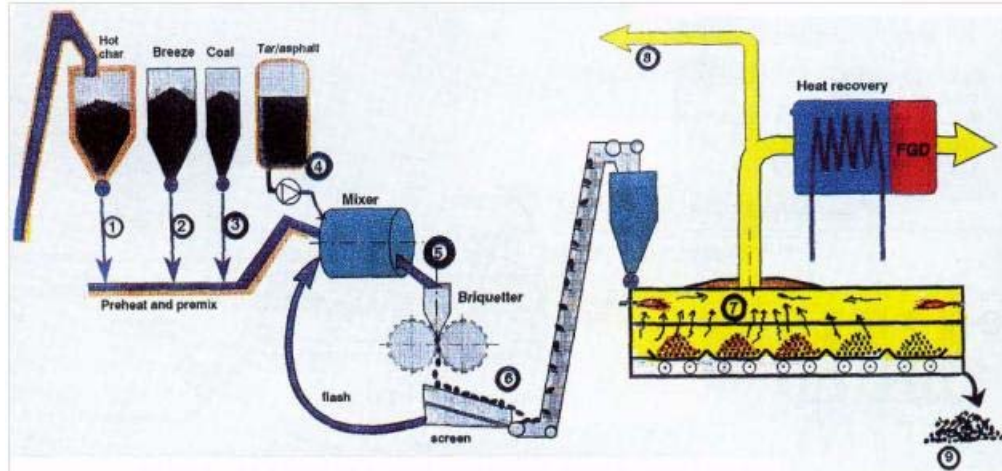


Figure 2.1 A continuous Form coke manufacturing Pilot Plant from Wolfe et al [6]

Early efforts to convert soft **brown coals** to coke by East Germany were unsuccessful due to the poor CSR/CRI and compressive strength. However, the coals were put to use to make a char type product (lignite coke) to provide active carbon for a various environmental applications. Another effort to produce furnace grade coke was by Cengizler et al. [7], wherein the char was mixed with a binder while being heated to 90°C, the resultant mixture was subjected to the briquetting process at 58.9 Mpa. The briquettes were then air-cured at 200-285°C to produce formcoke.

2.2 Process Description

The form coke process can be categorized in two general types, based on the origin of the starting materials. If the char and binder are obtained from the same source, the process is known to be a "Homogeneous Process". Whereas, if the raw materials used in the process are obtained from different sources, i.e. a combination different chars/coals and binder materials, then the process is said to be a "Heterogeneous Process" [8].

Binder products obtained from fossil fuels usually have a problem meeting environmental regulations [9]. Also, in a homogeneous type process, the char/tar yields heavily influence the form coke production. On the whole, the intrinsic properties of form coke depend on the properties of the char/ biomass, properties of the binder and overall processing conditions [10],[11]. An ideal form coke process viz. biocoke process, aims to be a "homogeneous process" in order to be more economically viable.

2.2.1 Process Conditions

Clark et al [11] investigated the relationships between the mechanical strength of the formcoke, the specific properties of the input materials and their effect on briquette density. Its magnitude in the case of solid feedstock properties is yet unclear. It is inferred that narrow size distributions of the raw material lead to lower briquette strength [12]; however, the increase in briquette strength due to the incorporation of high particle sizes is questionable. "Binder content" and "fluidity" are two important parameters expected to have an effect on the strength of form coke briquettes. Increasing the binder content enhances binder penetration within the pores [11],[13]. Ideally, the optimum range for the binder content is 12 -18 percent by weight [14].

2.3 Impact of the Form coke process

The conception of the form coke process brought upon a revolution in the coke-making industry. There is now a potential for developing a method of coke preparation to produce coke from sources different from metallurgical coal. However, from the above discussion, it is apparent that most of the form coke processes use fossil fuels in some capacity; i.e. either in the form of petroleum in pet coke, char obtained from crushing and

gasification of coal and coal tar which is also a result of the gasification process for the production of coke from metallurgical coke [15]. Therefore, there is a substantial possibility for the reduction of the GHG emissions.

Research is being done to develop a sustainable coke-making process which can utilize biomass based feedstock as raw material so that the produced coke (**Biocoke**) would be carbon neutral, sustainable and possess the qualities of standard metallurgical coke.

2.4 Biomass based Formcoke

2.4.1 Energy Act and the significance of Biomass based fuels

The form coke methodologies discussed above make use of the fossil fuel resources in their production. Since these resources are scarce and should be used in a moderate fashion, researchers are looking to develop novel ways to produce coke out of inexhaustible resources; the most common being biomass based raw materials. If sustainable technologies can be developed which make use of biomass sources like wood or agricultural and municipal wastes, industrial grade coke can be manufactured for the blast furnaces without depleting fossil fuels. Also, from an environmental standpoint, this would be beneficial considering the fact that biomass based fuels tend to have a less impact on the atmosphere.

However, to replace the prominent and high quality metallurgical coke with biocoke, The availability for a sustainable source of raw materials for production must be investigated. Due to the increasing dependence on foreign sources of crude oil, the United States Government , in a bid to reduce the gasoline consumption established the Energy Policy Act (EPact, P.L., 109-58) [16] in 2005 to reduce gasoline consumption.

The Renewable Fuel Standard (RFS) was created under the Energy Policy Act of 2005 and a mandate of renewable fuel was established. As per the regulations of the EPact, the RFS required 7.5 billion gallons of renewable fuel to be blended into gasoline in 2012.

The EPact was superseded by the Energy Independence and Security act of 2007 (EISA) [17] and expanded the blending of renewable fuel mandate to 36 billion gallons by 2022. The new fuel standard is sometimes known as RFS2.

2.4.2 Biomass Based Fuels

Research on the alternative fuels area is ongoing and as a result, biomass based ethanol and diesel are now commercially produced. Bioethanol is produced as a result of enzymic action through the fermentation of sugars and is claimed to be a substitute of gasoline. Biobutanol can be blended with regular gasoline in any ratio and can be used in a spark ignition engine.

Similarly, biodiesel is produced from the transesterification reaction of fat triglycerides (lipids) in which the fat molecules react with alcohol in the presence of acid/base to form fatty acid methyl esters (FAMES) [18]. However, biodiesel cannot be used directly and can only be blended with regular diesel to a maximum of 20% since it does not possess the same qualities like viscosity and inertness as the latter. It is known to react with the rubber gaskets and hoses causing damage to certain parts of the engine. Hence, the amount of biodiesel blended does not exceed the range 5-20%. Another important biomass based fuel envisioned to be a replacement for gasoline is biooil [19]. It is produced from the fast pyrolysis process of biomass using the destructive distillation in a reactor, followed by subsequent cooling. The principle is also known as biomass to liquid technology. The properties of biooil are somewhat different than gasoline in that it

contains a large amounts of oxygen and hence it cannot be branded as a hydrocarbon. Also, it has a very low heating value as compared to conventional fossil fuels. It is also very corrosive compared to gasoline. Its use in engines has not been successful. As mentioned earlier, research in the field of biofuels is ongoing and there is always the possibility for the emergence of new and more viable substitutes for fossil based fuels.

2.4.3 Evaluation of Feedstock

From the above discussion, it is apparent that the replacement of fossil fuels would require sustainable biological resources. Having recognized this fact, researchers at the United States Department of Agriculture, along with the Department of Energy and Oakridge National Laboratory has been working on the evaluation of sustainable biomass based resources and to find out whether the available biomass reserves are sufficient for the production of biofuels to replace the US gas and oil imports by 30%; a goal established by the biomass R&D Technical Advisory Committee [20]. The study concluded that with the available forest and agricultural land resources, a large-scale bio-refinery industry can be built, thus reducing the dependence on foreign oil and gas imports by producing biomass based energy sources which can replace fossil and other inexhaustible fuels with a little more than the fraction discussed above. It was concluded that the forest and agricultural land resources have the capabilities of establishing an industry for the bio-refinery with a capacity of approximately 1.3 billion tons of biomass.

This study has a huge impact on the future of the entire biofuel industry. The main challenge in gathering the biomass resources is to be cautious as not to cause an imbalance to the ecosystem. However, there are a certain species of trees in the southern

United States with a widespread presence and rapid growth rate. These trees can be put to a more productive use, such as the production of timber and wood pulp.

Loblolly, Shortleaf, Longleaf and Slash pines are the four main species of Southern yellow pines growing in the Southern part of United States. Despite the differences in the species, the wood of the different pines is almost indistinguishable with each other [21]. The Loblolly and the Shortleaf Pines are widespread across the state of Mississippi and can serve as feedstock for the production of biomass based fuels. The wood obtained from these trees is ideal for the production of biochar and torrefied wood.

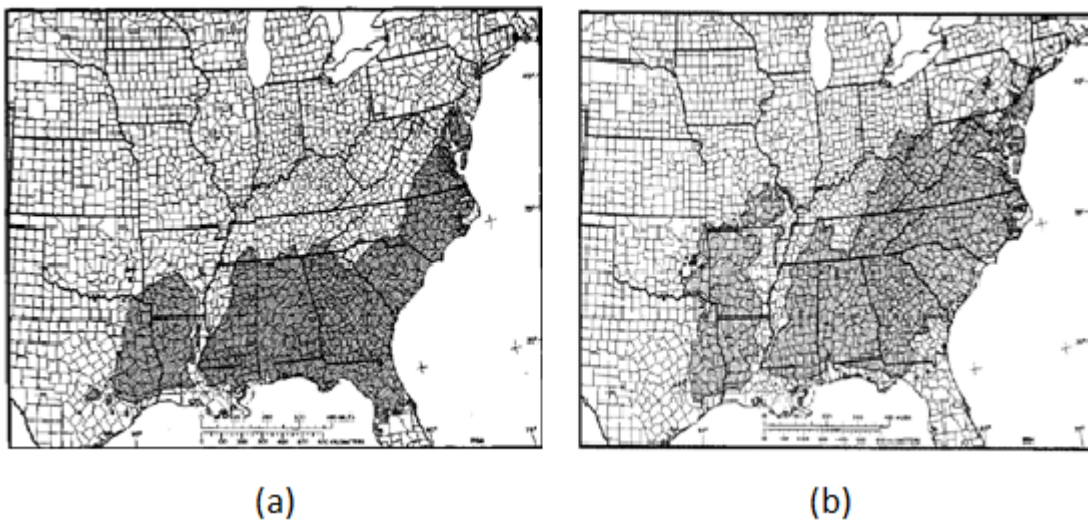


Figure 2.2 Growth Distribution of (a) Loblolly Pine , (b) Shortleaf [21]

2.4.4 Chemical Composition of Biomass

The chemical composition of the biomass is one of the influential factors for the selection. To obtain strong and stable biocoke specimens, feedstock with substantially more carbon content must be selected. nitrogen (N), sulfur (S) are responsible for the

occurrence of NO_x and SO_x emissions. Presence of chlorine (Cl) and sulfur (S) in the coke would result in the formation of deposits and are responsible for corrosion of any steel equipment in contact with them. An ideal biocoke specimen would be one with minimum ash content.

The ash content is an important factor and it effects the performance of the coke in the Blast Furnace. Hence, when selecting the raw material, it is important to recognize the presence of ash forming element like potassium (K), sodium (Na), aluminum (Al), iron (Fe) and phosphorous (P). These elements are detrimental to coke. Therefore, it is of utmost importance that to select a particular type of biomass as feedstock so as to minimize the effects of the components discussed above.

The European Committee for Standardization [22] published a document on the standards for the determination of ash content of Solid Biofuels wherein it provides data showing the chemical composition of various Wood and herbaceous sources. While the ash content of these biomass sources was determined on a dry basis; the major and minor ash components were measured in dry ash free conditions. Based on the information in the following tables, an informed decision can be made on the selection of biomass feedstock for the biocoke production process.

Table 2.1 and Table 2.2 illustrate the chemical composition of various woody and herbaceous biomass sources. As shown, the major components that determine the stability and the energy content of the fuel are the carbon (C), hydrogen (H) and oxygen (O). The nitrogen and the sulfur are the major emission producing agents (NO_x and SO_x), while chlorine (Cl) and fluorine (F) are responsible for the corrosion of the equipment in which the fuel undergoes combustion. Other influential chemical

components like ash and sodium (Na), potassium (K), iron (Fe), lead (Pb) and zinc (Zn) are the major and minor ash forming elements [23].

The ash content of the fuel influences the fly ash formation and the formation of ash deposits during the burning of the biomass. Therefore to minimize the ash storage and disposal, it is ideal for the ash content to be minimum. The major and minor ash forming elements are responsible for the fly ash emissions, ash melting and ash deposit formation. The presence of ash forming element increases the chances for slag formation in the furnace or a combustion chamber. Therefore it is desirable to have little or no ash forming elements to ensure smooth operation [23].

From the data presented in the above tables, it is apparent that the herbaceous biomass sources are richer in the corrosive and ash forming elements than woody biomass. Also the ash content is relatively higher in the former. Since both the biomass sources have approximately the same amount of C, O and H, it is more sensible to select woody biomass as feedstock for the production of biocoke. Also, it is interesting to note that the bark of the trees has significantly higher ash and ash forming elements. The bark captures the atmospheric dust and prevents it from getting into the wood.

Table 2.1 Typical mean values for the chemical composition of wood based fuels

Parameter/ Unit		Wood without bark		Bark	
		Coniferous	Deciduous	Coniferous	Deciduous
Ash	w-% d.b.	0.3	0.3	4.0	5.0
C	w-% daf	51	49	54	55
H	w-% daf	6.3	6.2	6.1	6.1
O	w-% daf	42	44	40	40
N	w-% daf	0.1	0.1	0.5	0.3
S	w-% daf	0.02	0.02	0.1	0.1
Cl	w-% daf	0.01	0.01	0.02	0.02
F	w-% daf	<0.0005	<0.0005	0.001	
Ca	mg/kg d.b.	900	1200	5000	15000
Fe	mg/kg d.b.	25	25	500	100
K	mg/kg d.b.	400	800	2000	2000
Mg	mg/kg d.b.	150	200	1000	500
Na	mg/kg d.b.	20	50	300	100
As	mg/kg d.b.	< 0.1	< 0.1	1	0.5
Cd	mg/kg d.b.	0.1	0.1	0.5	5
Pb	mg/kg d.b.	2	2	4	50
Zn	mg/kg d.b.	10	10	100	

Table 2.2 Typical mean values for the chemical composition of herbaceous fuels

Parameter/ Unit		Straw		Grains		Exhausted olive cake
		Wheat, rye, barley	Oilseed rape	Wheat, rye, barley	Rape	
Ash	w-% d.b.	5.0	0.3	4.0	5.0	2.0-7.0
C H O N S Cl F	w-% daf	49	50	46	63 7.5 25 4 0.1	48-50 5.5-6.5 0.5-1.5 0.07- 0.17 0.08- 0.15
	w-% daf	6.3	6.3	6.6		
	w-% daf	43	43	45		
	w-% daf	0.5	0.8	2.0		
	w-% daf	0.1	0.3	0.1		
	w-% daf	0.4	0.5	0.1		
	w-% daf	0.0005				
Ca	mg/kg d.b.	4000	15000	500 5000 1500		
Fe	mg/kg d.b.	100	100			
K	mg/kg d.b.	10000	10000			
Mg	mg/kg d.b.	700	700			
Na	mg/kg d.b.	500	500			
As	mg/kg d.b.	< 0.1	< 0.1	< 0.1		
Cd	mg/kg d.b.	0.1	0.1	0.05		
Pb	mg/kg d.b.	0.5	2	0.1		
Zn	mg/kg d.b.	10	10	30		

2.4.5 Southern Yellow Pine as Feedstock

Since Southern pine is widespread in the state of Mississippi, it is more feasible to use woody biomass in the form of wood chips, extracted from the pine trees with the bark removed. The wood chips can be subjected to torrefaction wherein they are heated to a temperature of about 250°C until the basic chemical structure breaks down to form torrefied wood, they can finally, undergo fast pyrolysis to produce pyrolysis oil and bio-char.

However, to set up a commercial scale biocoke production plant, an uninterrupted supply of feedstock should be attained. According to the 2005-2008 USDA Forest Service Data, there is a surplus of Southern Yellow pine in the United States; particularly in the Southern region, a total of at least 59000 *bone dry tons* per day [24]. With the proper infrastructure and planning, this surplus alone could supply sufficient feedstock for the plant.

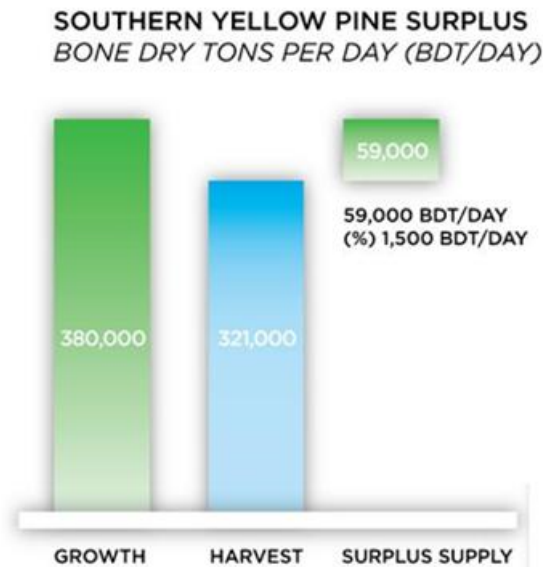


Figure 2.3 Bar chart showing harvest vs. growth (Southern pine) in *bone dry tons* [24]

2.4.6 Biomass Pretreatment Processes

Biomass is subjected to pretreatment processes before usage. The range of the pretreatment can vary from a simple washing, drying and grinding operation to thermochemical processing to breakdown the chemical constituents. The basic pretreatment operations, which can be performed on biomass are:

- i Washing: Presence of impurities on the surface of the biomass is responsible for contaminations when being subjected to thermochemical processing. Contact with soil or other external agents during extraction or transportation may be the causes for the presence of impurities on the biomass. Washing the biomass surface will remove most of the impurities and make it suitable for further downstream processes. Washing in hot water can dissolve some of the ash, particularly water soluble metals like sodium and potassium.
- ii Drying: Accumulation of moisture is one of the major concerns with the usage of biomass. Biomass which is freshly harvested can have moisture content of 60-85 by weight [25]. The process of heated drying can successfully remove most of the moisture from the biomass. The biomass may retain about 5-10 moisture by weight.
- iii Grinding: The surface volume ratio of biomass is one of the influential factors in determining the rate of heat transfer through the surface. Therefore, increase in the surface/volume ratio increases the rate of heat transfer. This is achieved by cutting or chipping the biomass to smaller dimensions. Also, the surface/volume ratio influences the bulk density of

the biomass. Therefore, decreasing the bulk density by grinding reduces the effort during long distance transportation. Once the wood chips are subjected to pyrolysis they become much easier to grind.

2.4.7 Thermochemical Processing

The thermochemical processes involve altering the chemical composition of the biomass by heating it at specific operating conditions, to produce specific products. The thermochemical processes are fast pyrolysis and torrefaction.

i Fast pyrolysis: Pyrolysis is defined as the thermal decomposition of organic material into liquid and solid chemical components at elevated temperatures in the absence of Oxygen [26]. The fast pyrolysis process occurs between a temperature range of 350-600°C at atmospheric pressure, most commonly in a Fluidizing Bed reactor. Since the residence time of the heat during a fast pyrolysis process is generally between 0.5-2s, extremely high biomass heating rates are necessary for the implementation of the process. The products of fast pyrolysis are bio-oil and biochar. To obtain a high liquid yield from the biomass into bio-oil, the process will require higher heat and hence will operate at the upper bound of the temperature range mentioned earlier. This is done by the introducing high temperature sweep gas into the chamber. The solid remaining as a byproduct of fast pyrolysis after complete de-volatilization is known as biochar. Biochar is low in density and its chemical composition is similar to that of charcoal [27]. To increase the yield of biochar, a different version of the pyrolysis process is adopted wherein the

operating temperature is between 300-400°C, with a longer residence time; in the order of hours.

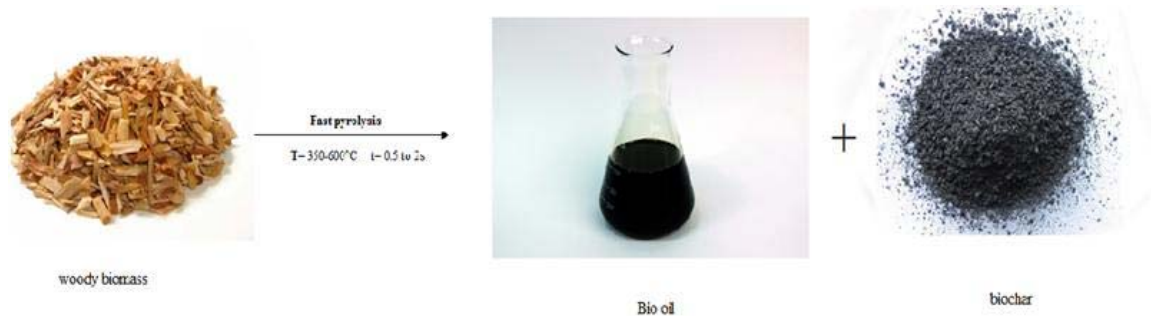


Figure 2.4 The Fast pyrolysis process

ii Torrefaction: Torrefaction is a mild pyrolysis process which involves heating the biomass in a reducing atmosphere between 200-300°C at atmospheric pressure. During torrefaction, depolymerization of the wood chemical structure occurs wherein the cellulose and the hemicellulose of the biomass are broken down thereby releasing moisture and other expendable volatiles, leaving a solid with a high heating value as the end product. Woody biomass, when subjected to the torrefaction process, the torrefied product can range from brown to dark black in color; when black in color, its properties are almost similar to some types of coal [28]. This greatly depends on the operating temperature and the residence time. The process can be performed at a wide range of residence times in the temperature range mentioned above. The operating temperature influences the extent of the depolymerization. Lightweight components

like CO₂, CO, acetic acid and methanol and other volatiles are the only compounds removed at lower temperatures. Higher operating temperatures lead to the significant depolymerization of the hemicellulose and cellulose present in the biomass, thereby making the biomass more brittle [29], easier to grind and lighter in weight. In addition to high energy density, the torrefied wood has low mass density and is hydrophobic in nature. It produces less smoke during combustion and has a high calorific value. Therefore it is an ideal choice as a raw material for form coke preparation.

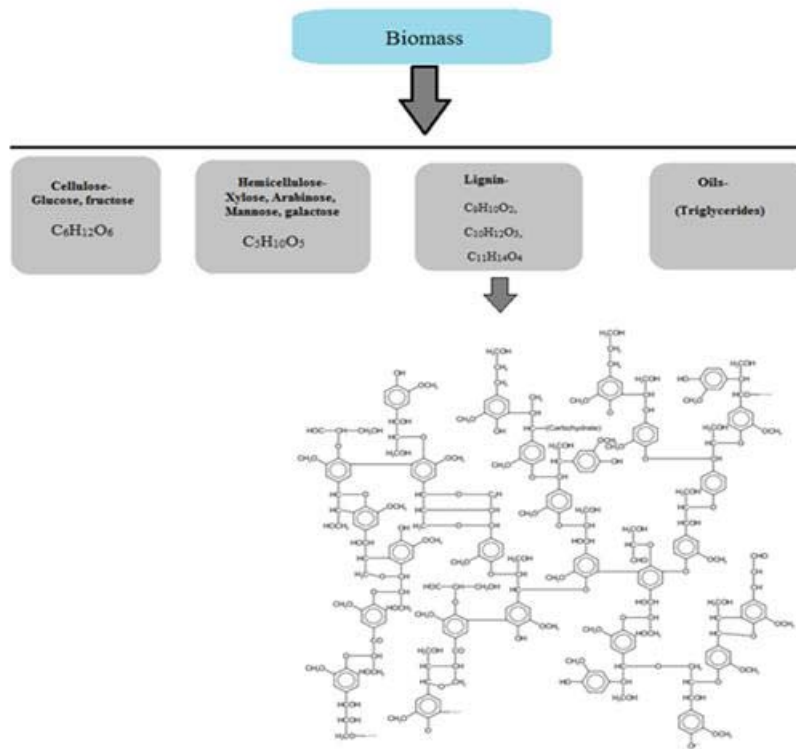


Figure 2.5 Chemical structure of biomass (lignocellulosic)

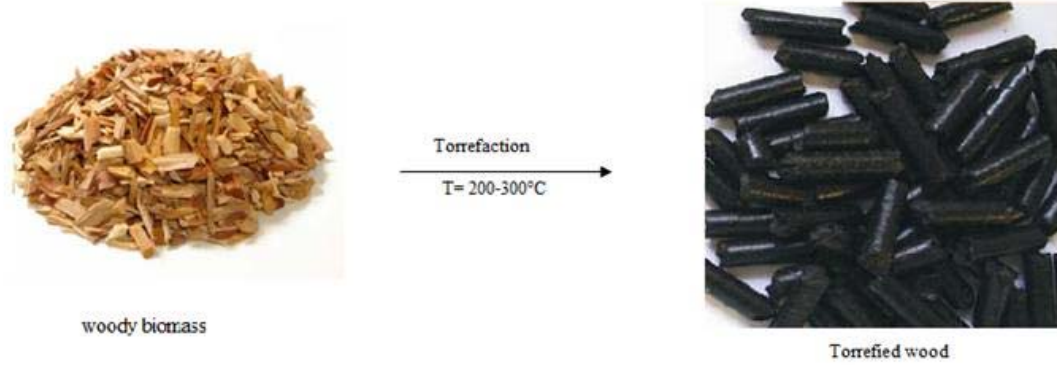


Figure 2.6 Torrefaction of woody biomass: Chemical Reaction

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CHAPTER III

EXPERIMENTAL METHODS

This chapter deals with extensive documentation, description of the research in the development of a biomass based coke alternative, which is carbon neutral and intended to be capable of becoming a commercial scale replacement to the depleting metallurgical coke supply. The biocoke production process was modeled after the form coke process, which was discussed in the earlier sections. The aim of this research was to develop a sequence of steps that would ultimately lead to the creation of a "recipe" for making biocoke specimens.

To check the compatibility of biocoke with the blast furnace, the biocoke test specimens are subjected to an industry standard test practice, known as the Coke reactivity Index/ Coke Strength after reaction (CRI/CSR) test. The test procedure follows the ASTM code of regulations and was developed by the Nippon steel company [1]. If the test yields favorable results, then there is potential for biocoke to be a worthy contender to replace metallurgical coke in the iron and steel industry.

The following sections detail the experimental setup for producing the biocoke test specimens as they attempt to capture the evolution of the research methodologies that lead to the currently observed preparation process. The process was tested on two different feedstocks and the resulting specimens are compared to help select one of them

as the ideal choice for biocoke production. Also, different configurations of the binder material are tested to fine tune the process to get specimens of higher density.

3.1 Outline of Research

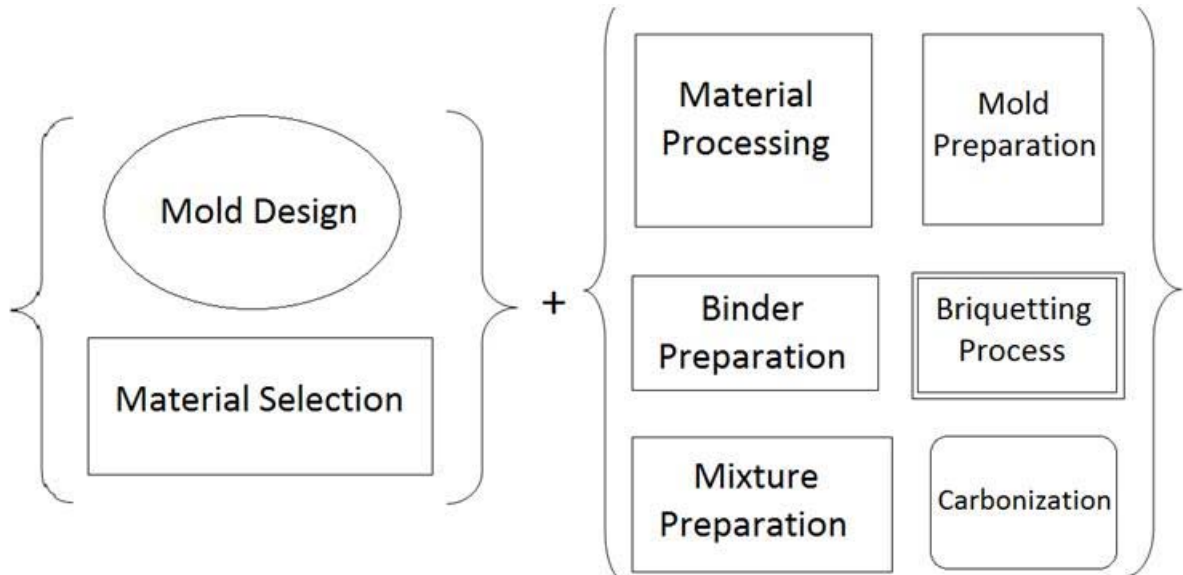


Figure 3.1 Flowchart outlining the efforts in the biocoke preparation

As described in the flowchart, initial efforts in the field of biocoke preparation were to develop the necessary equipment in which a biocoke specimen could be made. The materials in consideration for the feedstock were biochar and torrefied wood. However, in the above sections, it was established that biochar has up to 65-75% fixed carbon content with low ash and sulfur content. Therefore, even before the design of the mold, biochar was held favorable and was thought to have an edge over torrefied wood.

Since the objective of the research was to maintain an overall homogeneity in the process, *bio oil* was selected as the binder material. One of the reasons for the selection of *bio oil* as the binder was due to the fact that it contains a complex, highly viscous liquid

fraction known as *pyrolytic lignin*, which is used as an adhesive in the wood based panel industry [2]. From the above discussion, it is apparent that at a reasonable pressure and temperature the *bio oil* can fill the pores between biochar/ torrefied wood particles. The bio oil adheres to the surface of the torrefied wood, creating strong specimens. The bio oil does not appear to adhere to the biochar thus resulting in weak specimens.

Hence, it was concluded that the compression molding technique could present itself to be a viable option for the briquetting of the mixture, mainly due to the fact that a compression mold is used with a hydraulic press and can provide the necessary pressure to force the bio oil into the pores and also incorporate a way to supply heat to the process to cure the briquettes simultaneously. Hence the briquettes are known as green or uncoked briquettes.

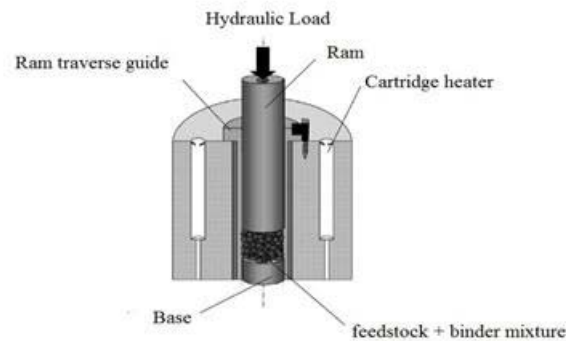


Figure 3.2 Compression mold concept

3.2 Mold Design

The following sections outline the concepts of compression molding, material selection, important design parameters, geometric modeling of the mold in **SolidWorks** [3], changes in design of the mold based on unsuccessful attempts to generate the

adequate pressures and temperatures in the mold. Let us now discuss the basics of compression molding.

3.2.1 Compression Molding

In compression molding, the charge or the molding compound is loaded into a cavity and is subjected to compressive loading most commonly achieved by applying pressure on the plunger. Most of the compressive mold designs allow for heating from within. While others rely on the presses in which they are used to provide the heat. These presses contain heating platens, which transfer the heat they generate to the mold via the conduction process. Some molds provide for the circulation of hot steam or oils through them to heat the molding compound [4].

A typical compressive mold has two halves. The upper half includes a ram or a plunger and the lower half is a mold cavity. The plunger usually has guide rods attached to it to facilitate the locking and releasing of the plunger. The molding compound is thus enclosed by the plunger and the mold cavity.

An ejector pin in the bottom of the mold allows for the easy extraction of the finished product without damage. Similarly, a variety of features can be incorporated in the design of the molds depending on the requirements of production.

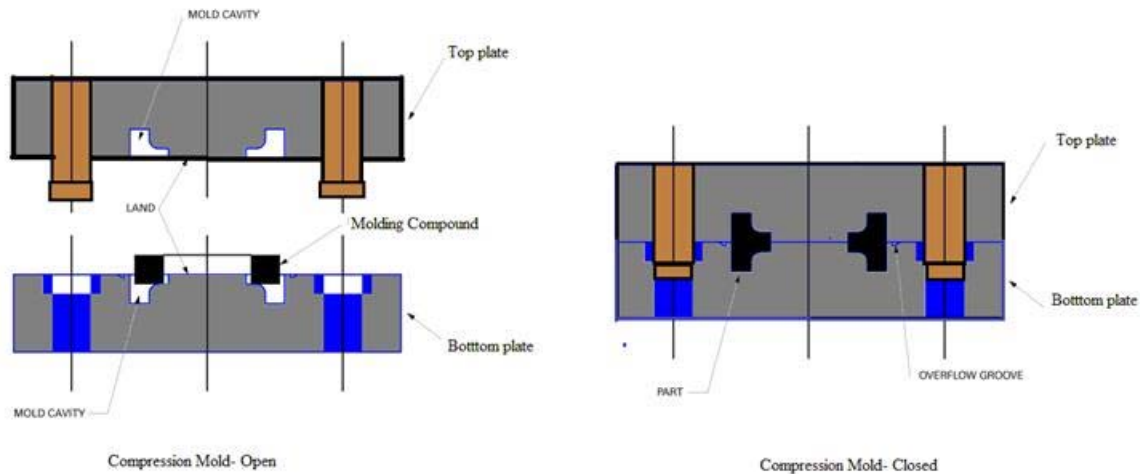


Figure 3.3 Compression mold with two mold cavities and guide rods

3.2.2 Mold Design: Geometric Modeling

The geometric modeling of the mold was done in **SolidWorks**. The mold has two main components: a *top plate*, which is mainly intended to allow for a steady transfer of the volatiles into the atmosphere, and a *bottom shaft/plate* containing the mold cavity. The bottom part of the mold contained the guide rods onto which the top part can be placed. The top plate is fastened to the bottom by two nuts. The nuts can be loosened at the end of the process for extraction of the specimen. Holes were also drilled in both the parts to allow for the placement of heaters. Separate holes were drilled in the top plate for the guide rods. A hole was also drilled at the base of the *bottom plate* for the placement of the small cylindrical slug, which serves as the *ejector pin*. A similar hole was drilled in the base of the top plate to allow the escape of the volatiles during briquetting the process. The parts were modeled individually and then assembled in **SolidWorks**.

3.2.3 Geometric Modeling using Solidworks

The design of the mold is generally done after evaluating certain parameters like, the size of the briquette, the material used in its fabrication, the list of parts to be made for the mold, the number of heaters required and their position, the position of the thermocouple holes, the values of clearance for critical parts, the quantity of raw material supported by the mold cavity.

Based on the maximum amount of raw material that can be fed into the mold cavity, the size of the mold was evaluated. Since the intended specimen shape is that of the frustum, the approximate volume of the mold cavity can be calculated by assuming that the mold cavity can hold around 150 gm of material. The density of the mixture is not known. Yu et al. [5] measured the physical and chemical properties of *bio oil* obtained from the microwave pyrolysis of corn stover and found it to be approximately 1.25 g/cc.

Therefore a conservative estimate of 1.25 g/cc for the density was adopted and the volume of the mold cavity was evaluated. Its value was found to be 120 cc. Also, the weight of the mold was not to exceed two pounds (2 lb.). The other dimensions of the mold were approximated, based on the volume of the mold cavity, the dimensions of the guide rods, and the desired positions of heaters and guide rods and the mass of the mold.

To model the bottom plate, a circle is drawn and extruded to create a cylinder. Then, a hole is drilled using the *Extrude cut* option to create the mold cavity. A draft angle is provided in the mold cavity to allow for the smooth removal of the finished specimen. A draft angle of 20° was provided to the mold cavity, thus changing the shape of the mold cavity from cylindrical to frustum. The bottom of the mold cavity is filleted,

to facilitate the removal of the briquettes. Holes are drilled for the inclusion of heaters and guide rods. Finally, the hole is drilled for the ejector pin. The drawing of the *bottom plate* is shown in Figure 3.4

The outer radius of the top plate is the same as the radius of the bottom plate. A disc is first created by extruding a circle with the radius equal to the outer radius. An inner circle is drawn and a 0.2 inch deep cut is made on either side of it so that a circular protrusion is formed on the either side in the form of a disc as shown in Figure 3.5. Two different groups of holes are drilled, the first four for the guide rods and the rest for the heaters. The groove facing the mold cavity is given a draft angle of 20°.

Three small holes are drilled in the mold configuration, one in the top plate and two in the bottom For the placement of thermocouples. They are placed in such a way that the functioning of the mold is not affected.

The bottom plate and the top plate are now assembled along with the ejector pin and the guide rods per Figure 3.6. The hole drilled at the base of the bottom plate is given the appropriate clearance for the ejector pin. The guide rods can be modeled in two different ways. They can either be extruded over holes or can be assembled later with an interference fit.

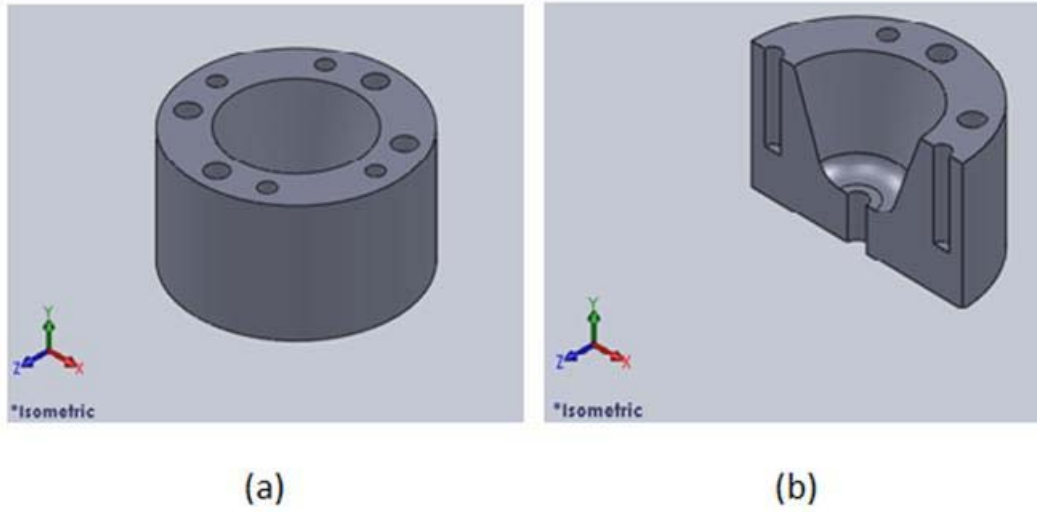


Figure 3.4 Isometric and section view of the bottom plate

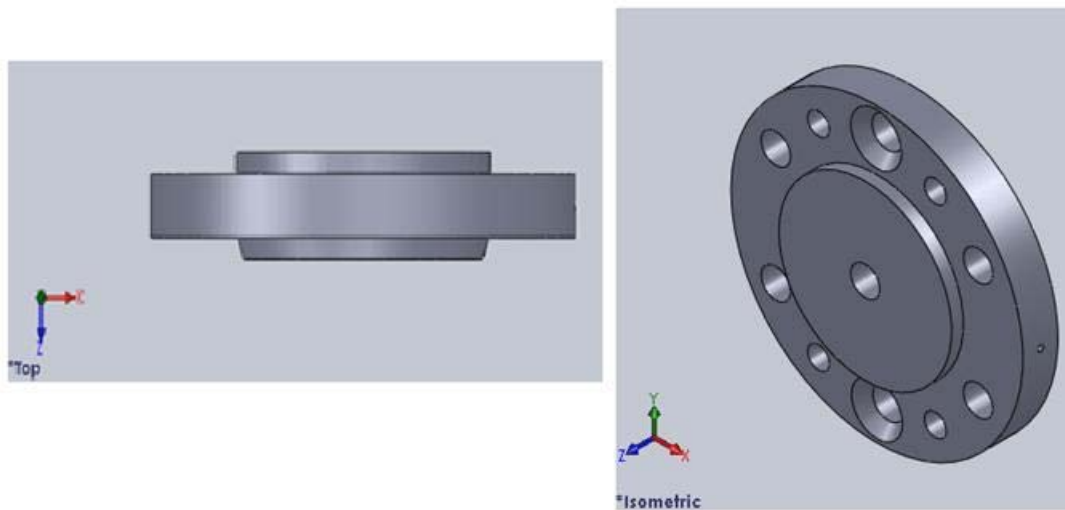


Figure 3.5 Top and isometric views of the top plate

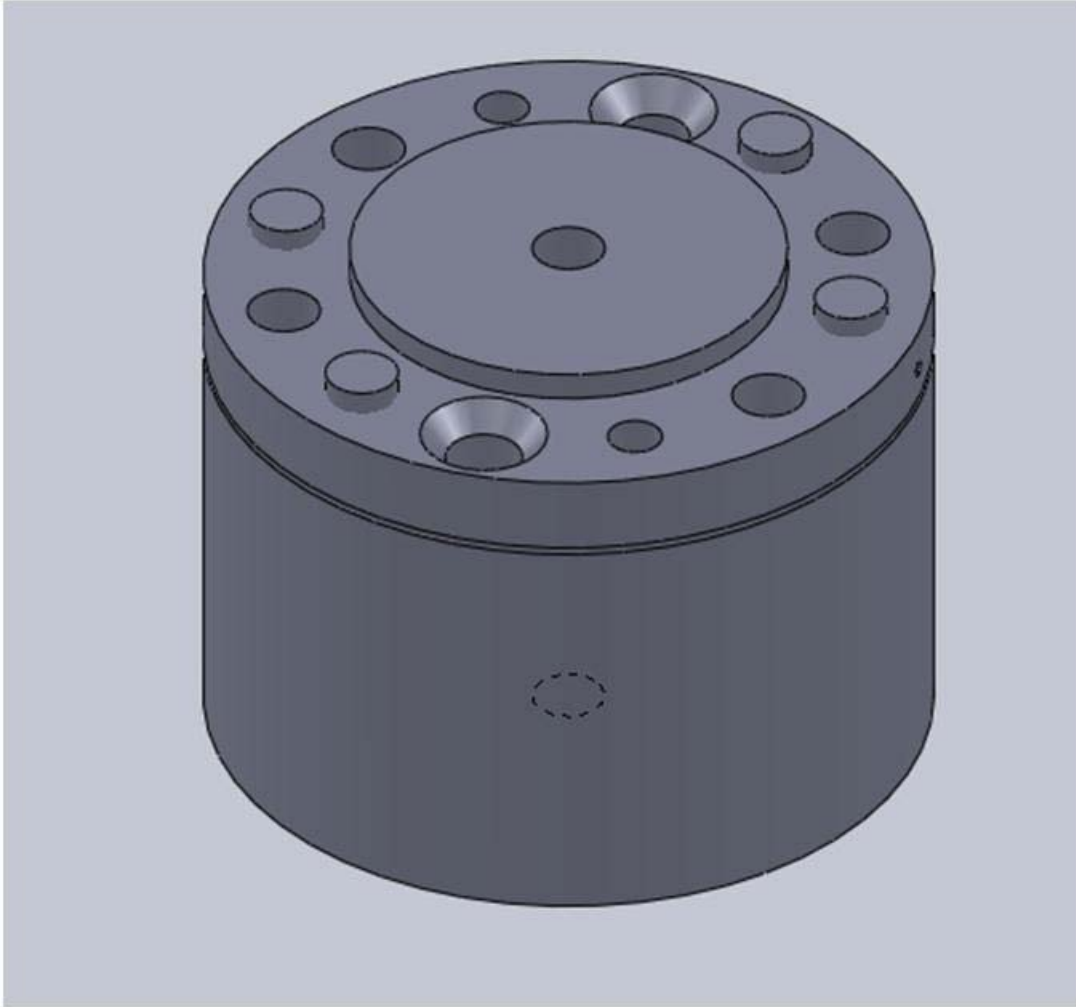


Figure 3.6 Isometric view of the assembly

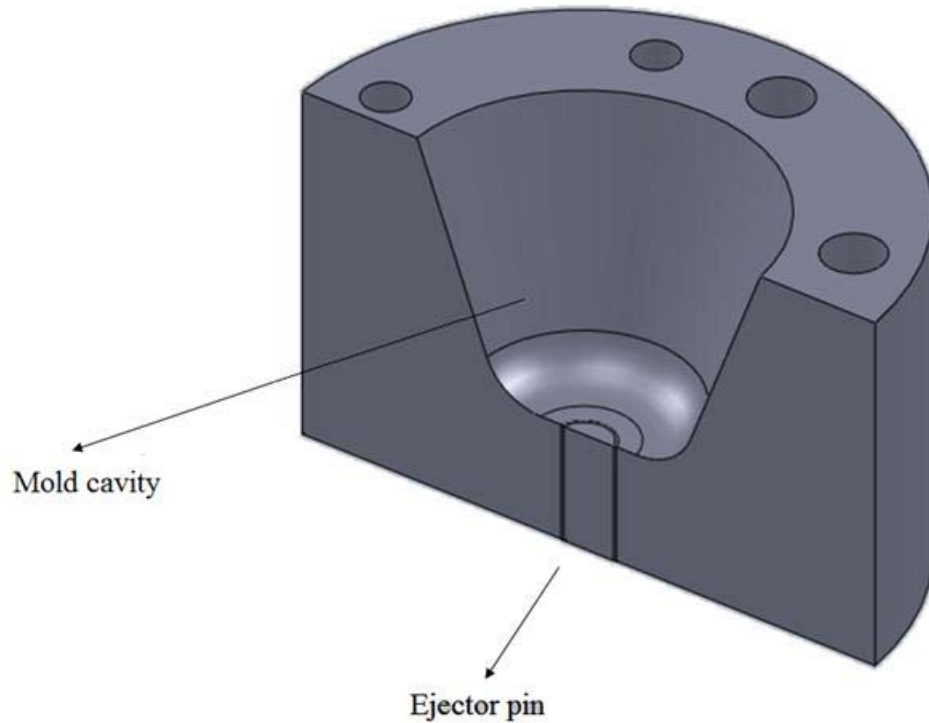


Figure 3.7 Section view of the bottom plate- ejector pin assembly

Two screws were used to attach the top plate to the bottom plate. Two 1/2 inch flat head socket cap screws were selected and the appropriate holes were drilled taking the countersink diameter and angle into consideration. After designing the mold, ASTM 4140 H.R.S steel was selected for fabrication.

However, the described mold configuration is not final. There are certain factors related to the further processes that resulted in changes to the mold configuration. These factors will be discussed in detailed in the following section.

3.3 Material Selection

The selection of the raw materials is one of the most important tasks in the biocoke production process. Proper care has to be taken in the materials as the raw

materials properties may affect the basic physical and chemical properties of the biocoke produced. Biomass which is devolatilized and depolymerized to certain extent is an ideal option for the starting material.

Therefore, as discussed in the earlier section, biochar and torrefied wood were in contention to be the raw materials. This is due to the fact that torrefied wood and biochar were previously used in making pellets with *bio oil* as the binder. The pellets were 1 inch wide and 1 inch tall and the average weight was 16 gm. They were made in a split mold configuration with a pressure of 5000 lb and temperature 302°F. The purpose for making the pellets was to examine the compression strength of the pellets [6]. The results of the compression strength test were quite interesting. The maximum pressure at failure was about 4000 psi for a specimen made out of torrefied wood and *bio oil*.

In addition to the results of the pelletization process, the physical and chemical properties of biochar and torrefied wood were discussed in detail in the earlier chapters. Also, the pretreatment procedures undergone by them were also detailed. The above discussion forms the basis for the selection of biochar and torrefied wood to be one of the raw materials in the biocoke production process.

3.3.1 Material Processing

The pretreated raw materials used in this process were procured from outside sources. However, the torrefied wood and the biochar are subjected to some amount of material processing. Due to the difference in the properties between the two materials, it is apparent that the parameters involved in the briquette production will differ based on the material selected. The torrefied wood that was used in the process was in the form of pellets. The average height of the pellet was about 0.5 inches.

The biochar obtained was crushed to an average particle size of 0.1 inches. The torrefied wood is also ground until a particle size of 0.1 inches is attained.



Figure 3.8 Ground torrefied wood and biochar powders

3.3.2 Binder properties

Bio-oil is a mix of organic components with a high water (15-30%) and oxygen content (35-60%). Because of the high water and oxygen content, it has a low heating value: 50% of the value for conventional fossil fuels [7]. However, The acidic nature of bio oil is the limiting factor for potential applications. There are certain compounds present in bio oil which evaporate as volatiles with the increase in temperature. Hence, bio oil is not very stable. The viscosity and the average molecular weight of the bio oil increases with time due to the expulsion of volatiles, thus resulting in phase separation [8].

However, the water insoluble part of bio oil has a substantial amount of pyrolytic lignin, which can be obtained from the fractionation process or by just ageing the bio oil. This is one of the reasons for selecting bio oil as the binder for the briquetting process. When mixed with the finely ground raw material, the bio oil was expected to harden over time as the temperature increases, thereby filling the pores of the devolatilized mixture. What really happens is that the bio-oil acts as a glue, gluing the fine material together.

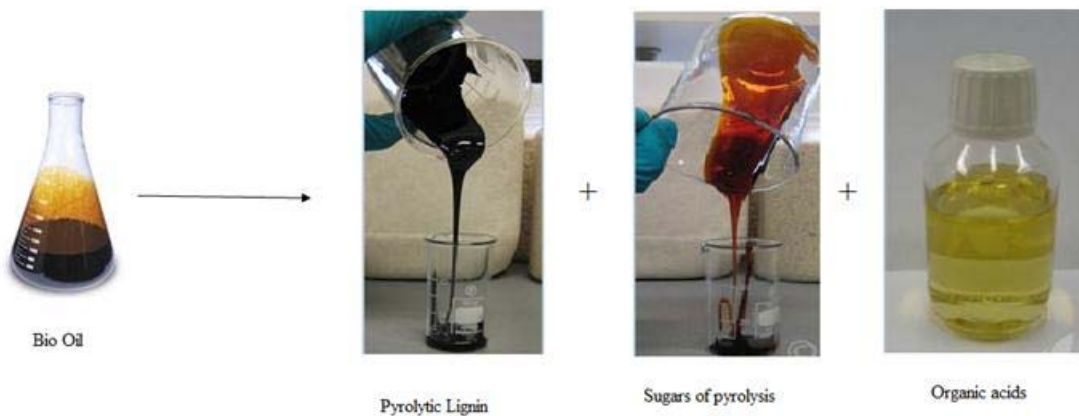


Figure 3.9 *Bio oil* and its constituents

3.4 Equipment

The experimental setup uses certain equipment. Since a compression mold is used for the briquetting purpose, a **CARVER**[®] [9] hydraulic press was installed. Due to budgetary constraints, a press with a heating platen could not be afforded. However, one solution to the problem is to provide the mold with an external heating source. The total number of heaters required to heat the mold was evaluated during the mold design by considering the mass of the mold, the wattage and dimensions of the heater. **OMEGATHERM**[®] [10] cartridge heaters were used to supply heat to the mold.

As the mold contained thermocouple holes at three different locations, A digital thermometer was used to measure the mold temperatures. An electrical system was designed with a provision to attach removable heater leads. A mold release agent, **Frekote**[®] [11] was used on the surface of the mold to avoid the bonding of external impurities with the mold.

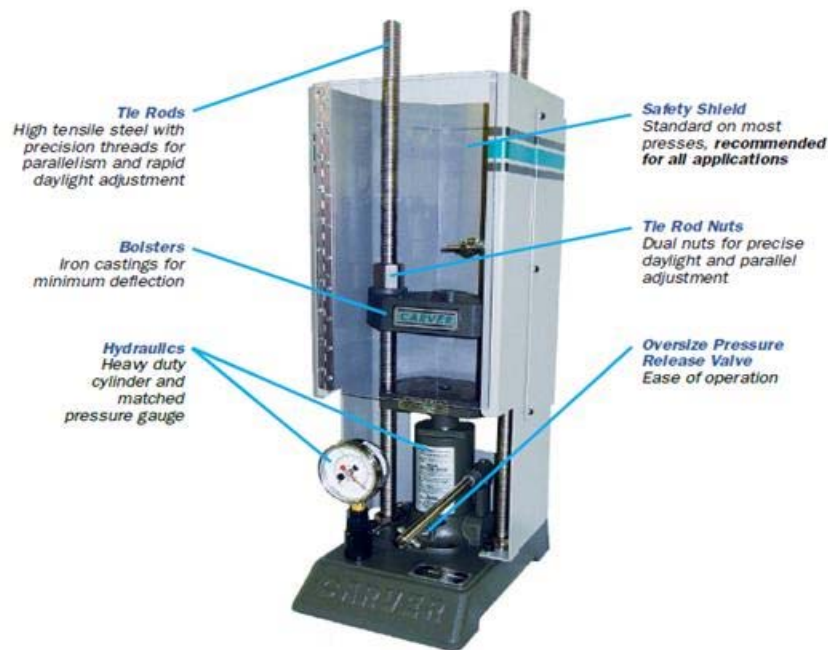


Figure 3.10 Carver Hydraulic press [9]

3.5 The briquetting process

The briquetting process adopted for the biocoke production is a bit different when compared to the briquetting of caking coals. In the hot briquetting process for the caking coal, if process is run for the production of a single specimen, almost all of the charge is shaped without the need for a binder. During such a briquetting process, the operating

temperatures are increased till the softening range is attained, at which the point the charge is shaped [12].

However in the biocoke experimental setup, the main goal of the hot briquetting process is to produce "green briquettes"; i.e., a lump of high density solid in which the biomass powder is fused with the *bio oil*. After the briquetting stage, the specimens are expected to have expended most of the constituent volatiles. Hence, in the field of briquetting of biocoke, the operating temperatures and pressures were relatively unknown during the initial stages of the research.

3.5.1 Initial stages: Process Formulation

During the initial stages of the research, the briquetting process was modeled after the biocoke pelletizing process described in the earlier sections. The operating pressure and temperature conditions used for producing pellets were adopted. The priority of the briquetting process was to produce an ideal specimen weighing 1/3rd of a pound i.e. close to 150 gm, based on the mold dimensions and its capacity.

During the initial feeding trials, 100 gm of mixture was prepared to be fed in the mold. For both raw materials biochar and torrefied wood, the material was ground to meet the respective desired particle size. They were then mixed with around 15% of the *bio oil*. However, after successive attempts, the maximum quantity of the mixture that could be fed in the mold was found to be around 55 gm.

Consequently, on a trial basis, the briquetting process was tried on the feed material by operating the hydraulic press on the mold. The mold was heated till the maximum temperature reached 150°C at the operating pressure of 5000 psi. When the maximum temperature was attained, the heaters were turned OFF. After the temperature

of the mold reached room temperature, the top plate was removed to investigate the outcome.

It was observed that the biomass mixture had not been cured and hence, the process was unsuccessful. The contents of the mold were removed for further examination. It was observed that mixture was relatively dry and quite porous. Moreover, a great deal of scraping was required for the material removal due the presence of deposits on the surface of the mold cavity. Also, due to the size of the mold and its weight, the time required for the heating of the mold to the maximum temperature specified above was relatively longer for the material process.

However, the results of the preliminary attempts at briquetting helped answer some of the important questions in the process. The problem or *issues* identified during the preliminary attempts were: the high mold heating time, the inability of the mixture to be cured, the very small amount of mixture that can be fed into the mold and finally the residual deposits on the surface of the mold cavity. The following sections deal with the ways in which these obstacles were overcome:

The sequence of events undertaken in the preliminary process were retraced to get a better idea. This started with a casual measurement of temperature of the elements surrounding the mold. The objects directly in contact with the mold were the platen on the base of the press. Therefore, the temperatures of the platen and the base of the press were measured with the digital thermometer. Also the temperature of the bolster, which is a iron casting meant for deflections [9], was measured. Hence, it was deduced that heat is being transferred out of the system rapidly from the bottom and the top.

To prevent the heat transfer phenomenon, the contacts between the mold and the platen, between the platen and the base of the press were removed by placing washers between them. The mold was hence standing on a three washers, two of which were kept on the vertices of a side of the platen. The third washer was placed perpendicular to the mentioned edge thereby forming a triangle. Also, the exterior of the mold was wrapped in aluminum foil to provide insulation.

Since there was a problem with the removal of material from the mold cavity, it was also lined with the aluminum foil. The heat transfer in the mold was examined by conducting a test on the mold. The mold was heated to measure the time taken to reach the maximum temperature. As it took less time to heat the mold, it was concluded that the heat transfer from the mold surface has been minimized. This was confirmed by measuring the temperatures of the surfaces measured earlier.

A bold assumption before the designing of the mold was that, the intensive pressure conditions developed due to the devolatilization of the mixture during heating would help in generating a load in the direction of the hydraulic load. Hence the top plate had a 0.2 inch extrusion which was meant to transfer the pressure created by the hydraulic load to the mold cavity. Since an extrusion with only a 0.2 inch depth would mean lesser cost for making the *top plate*, the top plate was modeled in the said configuration.

After the attempts to make a specimen after solving the heat transfer problem failed; it was deduced that the inability of the top plate to transfer the pressure applied by the press to the mold cavity was the reason for the lack of any sign of solidification in the specimen. At this point, two important changes were made to the experimental process.

Since the top plate was contributing substantially to the heat transfer problem, the inability to apply any pressure on the specimen prompted for finding an alternative to the top plate. The maximum temperature to which the mold is heated was increased to 420°F (200°C) and beyond. The operating pressure remained the same as discussed earlier.

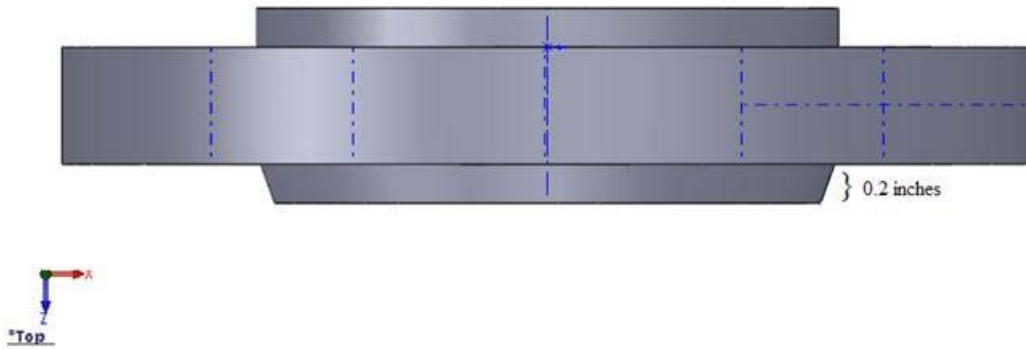


Figure 3.11 Figure showing the depth of the extrusion provided for ramming action

3.5.1.1 Top plate issues

As a substitute for the top plate, a cylindrical block 2.5 inches in diameter and 2 inches in height was used. This block was made out of wood and served as a ram for the briquetting process. Since there is potential for sticking of the mixture to block during the process, the block was wrapped in aluminum foil. The ramming potential of the block was examined by compressing the mixture in the mold cavity, in the absence of heat. On examination, it was observed that the transfer of pressure from the press to the mold cavity was relatively efficient.

With the removal of the top plate, the heat transfer issue was resolved without the need for wrapping the mold with the aluminum foil. However, the process of lining the mold cavity was retained to prevent material deposits on the mold surface.



Figure 3.12 Wooden block wrapped in Aluminum foil

3.5.1.2 Specimen Extraction and Mixture Preparation

A washer was placed inside the mold cavity to facilitate for the specimen extraction. When force is applied on the ejector pin, the washer distributes the pressure uniformly onto the specimen so as to avoid issues like breaking of the briquettes due to high stress concentration.

Also, it was discussed earlier that the reason for selecting *bio oil* as the source for the binder was the presence of *pyrolytic lignin*, a highly dense resinous compound which has adhesive properties. However, the *bio oil* on the whole is a highly watered down substance. Therefore, when the temperature of the mold reaches the boiling point of water, the mixture is devolatilized leaving very little residue of the *bio oil*. Consequently,

pyrolytic lignin was prepared separating the water insoluble components with the help of the ageing process which was discussed earlier. This helped in securing a more concentrated and sticky binder for the briquetting process.

3.5.1.3 Feeding Process

The only issue with the briquetting process at this stage was a need for developing a feeding process which can feed more material. Therefore, an alternate feeding process was conceived during the time when the cylindrical block was tested for its ramming potential. If the mixture was fed in different stages, there was a potential for maximum input. In every stage the material is fed, the mold cavity is subjected to a pressure by the press so that more space can be created in the mold cavity for further mixture input.

The feeding process was therefore divided into three stages. In every stage, mixture is fed under pressure. The pressure applied during the feeding stages was given in a decreasing magnitude and the pressure was maintained between 660-1100 psi. For example, in obtaining a torrefied wood specimen weighing 74.3 gm, a 100 gm of the mixture was prepared in which the percentage of ground torrefied wood powder was about 70% of the total weight. The mixture also included 20% of *bio oil*, the rest being *pyrolytic lignin*.

Based on this feeding principle, both biochar and torrefied wood specimens were tried. The mass of all the specimens produced were in between 50 and 88 gm, with the average mass being 70 gm. The now modified briquetting process was more favorable in the production of briquetted of torrefied wood as the raw material rather than biochar. This was evident from the results of the briquetting process which will be discussed in the following chapter.

Also it should be noted that the steps discussed and the specimens produced till now are a result of fine tuning the briquetting process over a long period of time. The ultimate goal of the research carried out for the thesis was to produce briquettes weighing an average weight of a 100 gm.

One major disadvantage of the removal of the top plate is the rapid expulsion of the volatiles. Due to the multiple feeding stages incorporated into the briquetting process, the resultant pressure on the mold cavity is somewhat higher than before. Due to this, the volatiles are expended at lower temperatures in higher quantities. Also, the structural integrity of the specimen is compromised and unwanted breakage occurs.

Therefore, there is a need to fine tune the feeding process so that more material is delivered into the mold at lower pressure conditions. To achieve that goal, further changes in the mixture feeding process and the mixture composition were made, the details of which will be discussed in the next section.

3.5.2 Final briquetting process

A final working model for the briquetting process was developed based on the experiences described in the above section. The issues related to feeding and mixture composition were solved so that specimens of higher mass can be produced.

A detailed discussion on the final briquetting process is given below:

3.5.2.1 Mixture preparation

To produce a green briquette using the final briquetting process, the torrefied wood pellets are finely ground to a powder with a particle size of 0.1 inches. The feeding process was improved in such a way that a total of 131 gm of wet mixture can be

accommodated into the mold. The details involving the feeding process are described in the "mold preparation" section. The binder used for the preparation of the mixture was a combination of *bio oil* and *pyrolytic lignin* much like the previous iterations. However, their respective quantities are different. This change was incorporated into the process because it was observed from previous endeavors, that *pyrolytic lignin* played a more significant role in the briquetting process than *bio oil*.

Therefore, the mixture was prepared accordingly. From the 131 gm total weight of the mixture mentioned above, the amount of torrefied wood used is between 70-75 % of the overall weight, much like the previous iterations. The quantities of the *bio-oil* and *pyrolytic lignin* however were reversed i.e. the amount of *pyrolytic lignin* used was in the order of 19-23% and the amount of *bio oil* used was below 8%. The torrefied wood powder and the binder are thoroughly mixed in a bowl before being fed into the mold.



Figure 3.13 Mixing of bio oil, pyrolytic lignin and torrefied wood

3.5.2.2 Mold Preparation

Before feeding the mixture into the mold, a certain degree of mold preparation is required. **Frekote®** is sprayed on the outer surface of the mold and in the mold cavity and

the mold is left to dry at room temperature for 10-15 minutes. The insides of the mold cavity are lined with the aluminum foil. For this, the foil is folded and arranged on top of the washer. The length of the foil is adjusted so that the foil extends beyond the starting point of the mold cavity. This will provide more volume thus allowing more material to be fed into the mold cavity as shown in Figure 3.14. After the mold is prepared, the next step in the briquetting process is the feeding of the material which is discussed in the following section.

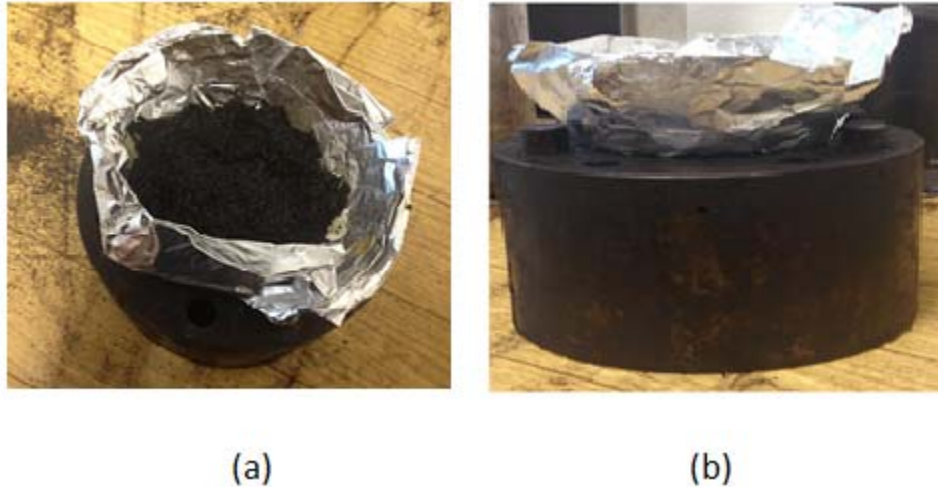


Figure 3.14 Feeding process and mold preparation

3.5.2.3 Briquetting Process Operation

There are two levels of operation at this point in the process, they are: feeding the material into the mold and thermal and mechanical loading of the mold in the hydraulic press. After the mold is prepared for the feeding process, the mixture prepared in the quantities mentioned above was fed into the mold in two stages.

In the first stage, the mold is subjected to a pressure of 885 psi. When the pressure in the press is released, the mold is taken out for the next stage of feeding; in which the mixture remaining after the first feeding stage is transferred into the mold subjected to a pressure of 710 psi. The maximum pressure of the second feeding stage becomes the operating pressure in the actual briquetting process.

After the mixture is completely loaded into the mold, the heaters were placed in the heater holes present in the mold and the electrical unit is turned on. The operating pressure is maintained at 3400 lb till the temperature of mold reaches 302°F. Beyond that mark, the pressure is allowed to decrease to around 330 psi, but it is maintained at that pressure till the maximum temperature of about 420°F or more, is attained. The mold is then allowed to cool by disconnecting the leads of the heaters and shutting down the electrical system.

At around 280°F, the mold is released from the press and the green briquette specimen is extracted. The aluminum foil present in the mold cavity is deposited on the surface of the specimen per Figure 3.15. The residual aluminum can be easily removed with a pair of tweezers. The green briquette thus obtained is subjected to carbonization.



Figure 3.15 Torrefied green briquette with aluminum foil deposit

3.6 Carbonization

The green briquettes produced as the result of the experimental briquetting process are devolatilized to the maximum extent but the chemical composition of the solid is still rich in polymer compounds. This is due to the low operating temperatures of the briquetting process. This is due to the fact that the purpose of the briquetting process was to cure the mixture. The carbonization is the final process which will ultimately produce the bio coke specimens. The concepts of the carbonization process are discussed in detail in the next section.

3.6.1 The General Carbonization Process

The carbonization process forms the crux of the any coke production process. It involves the heating of coal or coal like substances at elevated temperatures between 1000-1100°C in an oxygen deficient environment [13]. The essence of carbonization is the depolymerization and the devolatilization of the charge; which, in the case of the form coke process is the products obtained after the briquetting stage. Usually, the coal charge is dried, pulverized and blended with oil before being fed into the coking oven or furnace. However, in the form coke process, since the binder is already present in the briquettes, the pre-treatment stage is unnecessary.

The briquettes are transformed into coke in three different heat regimes. As the heat travels from the heated inner wall to the coal charge/briquettes, the following heat regimes are developed:

- i from 375°C to 475 °C: Decomposition in the form of depolymerization and devolatilization occurs leading to the release of volatiles like water (H₂O), carbon-di-oxide CO₂ and other compounds of carbon and oxygen. The surface of the briquettes/coal charge becomes a little plastic in nature.
- ii From 475°C to 575°C: Evolution of aromatic hydrocarbons, wood tar from the form coke and binder compounds, leading to the solidification of the plastic charge into a semi-carbonized mass.
- iii From 600°C to 1100°C: This heat regime brings upon a significant change in the, weight of the charge, the percentage of carbon in the charge, structural stabilization of the coke, final evolution of hydrogen. This leads to the formation of a lump of solid with carbon content greater than 95%.



Figure 3.16 Pilot scale coke oven plant

3.6.2 Biocoke Carbonization

The carbonization process for the green briquettes was done in a small capacity electrical furnace at the Center for Advanced Vehicular Systems [14], the process was carried out in two attempts. The specimens produced from the previous iteration of the briquetting process and weighing between 60-75 gm were carbonized in the first attempt. In the second attempt, the specimens produced from the recent and final briquetting process were carbonized.

The carbonization process was undergone as follows. After the specimens are placed in the furnace, the furnace lid is closed and the specimens, in the presence of *nitrogen* are heated to a temperature of 100°C and their weights are measured. The temperature is then increased to 1100°C. This is done by raising the temperature in the furnace by 200°C every hour. After the said temperature is attained, specimens were

made to dwell i.e. the temperature was maintained at 1100°C for 6 hours. After the dwelling process, the heaters are turned off until a temperature of 100°C is reached. The heaters maintain a temperature of 100°C until the weights of the carbonized specimens are measured.

The carbonized specimens shown in Figure 3.17 are the biocoke samples produced from the biocoke experimental setup.

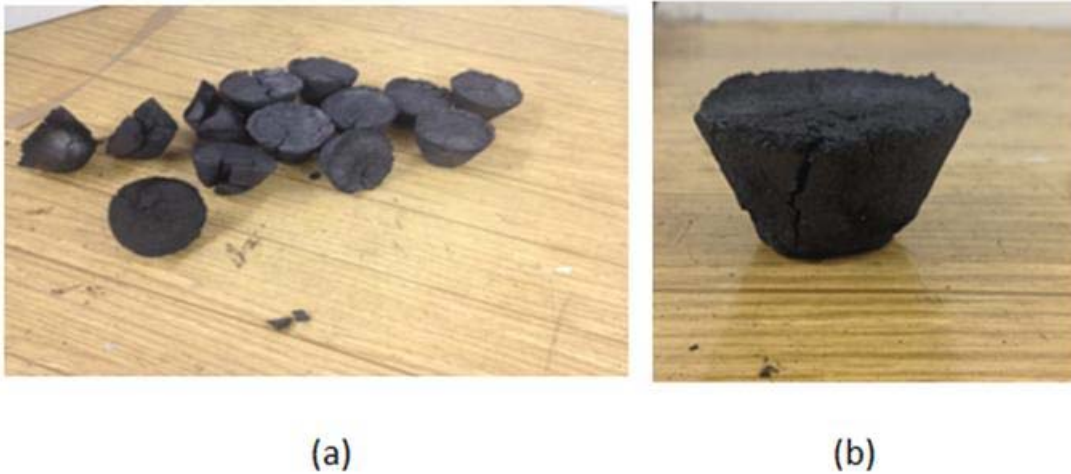


Figure 3.17 Biocoke specimens after (a) carbonization. (b) Biocoke single specimen

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CHAPTER IV

RESULTS AND DISCUSSION

The main objective of the research conducted for the purpose of this thesis was to develop an experimental setup to produce "briquettes" out of biomass and bio oil products was successful. The briquetting process developed not only cured the mixture that was fed prior to the process, it also was able to produce high strength specimens.

Based on the specimens developed from the briquetting process, various process parameters involved in the process were recognized and a working range for these parameters was established. The briquetting process was successful in creating specimens for the torrefied wood based biomass mixture. The results of the briquetting process for torrefied wood and biochar are discussed in the following sections.

4.1 Briquetting with torrefied wood as the raw material

The briquetting process yielded favorable results with the torrefied wood, in the sense that the curing process was successful. Since the process was being developed from the start, a lot of fine tuning had to be done in order to identify the relationships between the various parameters and how they affected the briquette formation. The tuning of the result was possible only because of the number of specimens that were produced from the process. It was discussed in the earlier sections that the feeding process was modified to

accommodate more charge into the mold. To better understand the significance of this change, let us compare the specimens belonging to the respective feeding process.

Table 4.1 and Table 4.2 point out a considerable change in the specimen sizes and dimensions. It is apparent that the higher outer diameters of the specimens in the first table was due to the fact that the new feeding technique provided more contact surface between the ram and the mold cavity. The mass of the specimens in the first table is in agreement with the above statement. The readings of the second specimen in the first table are rather unconventional due to the fact that the specimen broke at 1/4th of the total height and the bottom piece (which weighed 23 gm) was not considered since the broken piece was not carbonized. Hence its inner diameter is higher than the rest of the specimens because the value for taken at the point of breakage.

All the specimens in Table 4.1 had similar values for the amount of mixture transferred into the mold and the pressures at which they were fed. The total mass of the mixture fed into the molds was between 120-135 gm.

The 7th and 8th specimens mentioned in Table 4.2 have comparatively higher mass than the other specimens. This is due to the fact that a multistage feed process was employed for their production, whereas readings of the remaining specimens are fairly normal. However, based on the readings described in the first and second tables, it is apparent that the specimens produced by employing the multistage feeding process have higher densities compared to the other specimens.

Table 4.1 List of specimens with maximum temperature of operation after change in feeding process

Sample No.	Mass of the specimen, M (gm)	Height of the specimen, H (inches)	Outer diameter, D1 (inches)	Inner diameter, D2 (inches)	Maximum temperature, T (°F)
1	102	1.65	2.6	1.7	434
2	76 (+23)	1.3	2.5	1.9	420
3	100.6	1.6	2.65	1.6	430
4	112.3	1.8	2.7	1.7	436
5	94.7	1.6	2.6	1.6	430
6	94	1.6	2.6	1.6	431
7	95.7	1.5	2.6	1.6	428
8	86	1.45	2.6	1.45	424
9	98.8	1.7	2.7	1.6	420
10	93.4	1.55	2.6	1.55	419
11	118.4	1.9	2.7	1.5	453
12	83.6	1.5	2.5	1.5	418

Table 4.2 List of specimens with maximum temperature of operation before change in feeding process

Sample No.	Mass of the specimen, M (gm)	Height of the specimen, H (inches)	Outer diameter, D1 (inches)	Inner diameter, D2 (inches)	Maximum temperature, T (°F)
1	65.9	1.15	2.4	1.7	430
2	63.6	1.2	2.4	1.8	459
3	74.3	1.3	2.4	1.7	420
4	63.8	1.2	2.4	1.7	425
5	71.3	1.3	2.4	1.69	401
6	52.2	1.1	1.8	1.6	434
7	88	1.4	2.45	1.7	440
8	81	1.3	2.4	1.7	436
9	68.7	1.3	2.4	1.7	423
10	74	1.3	2.4	1.7	418

The details of the parameters during the briquetting process are mentioned in the Table 4.3. It illustrates the relationship between the mass of the specimens and their respective operating conditions for 8 of the best specimens under the final briquetting process. It was described earlier that in the final briquetting process, the quantity of the pyrolytic lignin used was greater than that of bio-oil.

Table 4.3 Operating conditions of 8 best specimens

Specimen No.	Specimen mass, M_o (gm)	Mass of input materials (gm)*			Pressure Conditions (psi)**			Maximum operating temperatures (°F)
		M_T	M_P	M_b	P_1	P_2	P_E	
1	118.4	102.8	31	11	862.00	545.97	198.93	453
2	112.3	97.6	30	14	851.00	563.66	243.14	436
3	102.0	94.5	28	11	773.65	583.55	176.83	434
4	100.6	89.6	28	14	669.76	663.13	265.25	430
5	98.8	87.8	26	17	663.13	674.18	198.93	420
6	95.7	86.0	24	20	685.23	656.49	353.66	430
7	94.7	84.7	23	16	811.22	676.39	287.35	428
8	94.0	87	15	21	762.59	618.92	309.46	429

*where M_T, M_P, M_b stand for the Masses of the torrefied wood, pyrolytic wood, bio oil respectively

**where P_1, P_2 and P_E denote the Initial feed pressure, the operating pressure and the pressure at the time of mold release

The relationship between the mass of the specimens and the various operating conditions are represented in the Figure 4.1, Figure 4.2 and Figure 4.3.

The figures describe the relationship between the specimen weight vs. the main operating parameters, i.e. the pressure and temperature. The graphs 4.1 and 4.2 indicate that the increase in the pressure conditions during the briquetting increases the density of the resultant. This was actually observed in the specimens 1 and 2 described in Figure 4.3. However, the overall pressure must not be high as this may cause the specimen to break. Figure 4.1 and Figure 4.2 seem to suggest that there should be a balance between the feeding pressure and operating pressure, i.e., the feeding and operating pressures must not affect the overall pressure of the system during operation.

Also, from Figure 4.3, it is suggested that the specimen weight may increase with the increase in temperature. But, experimentally, this was found to be true in the cases, where the quantity of the input materials was high. As seen in the above graph, two specimens 1 and 2 from Table 4.3 were obtained at higher temperatures. This may be because the time taken for curing the heavier specimens is more compared to the specimens with lower input mass thereby requiring higher temperatures

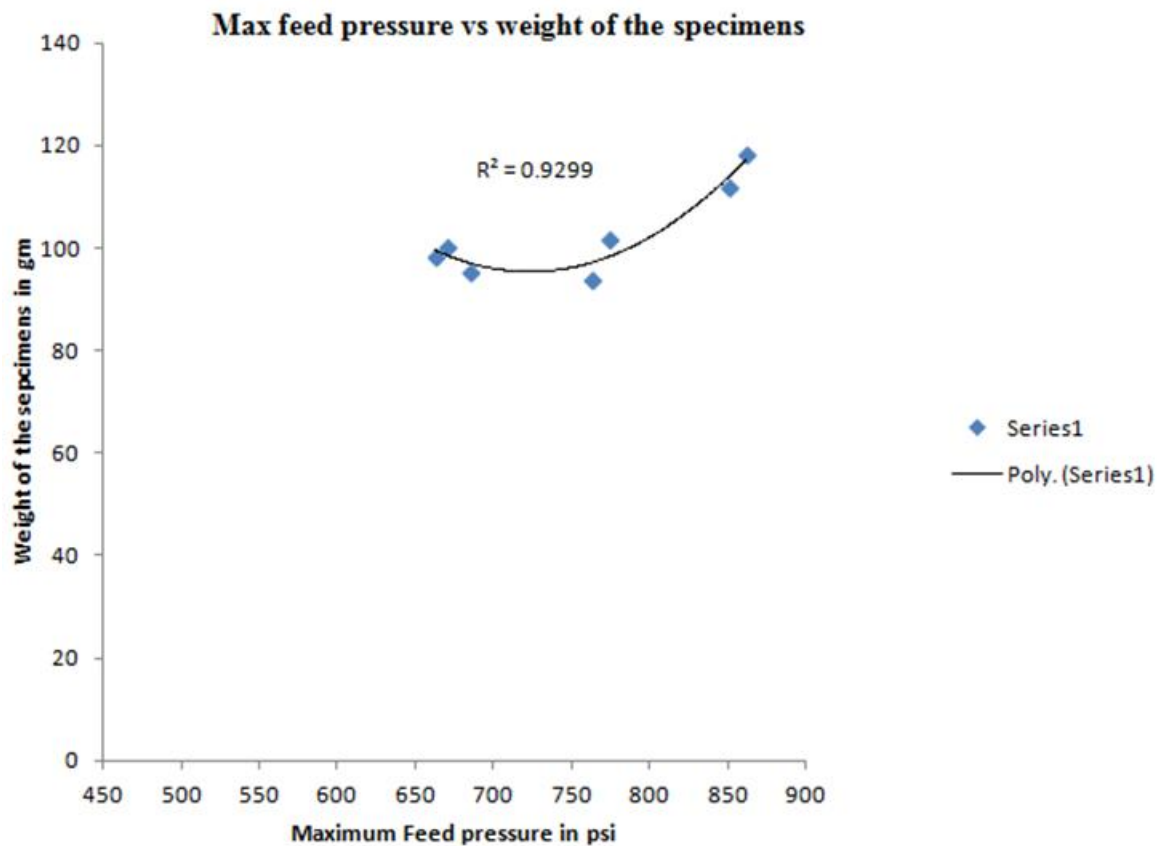


Figure 4.1 Graph showing relationship between P_1 and M_o

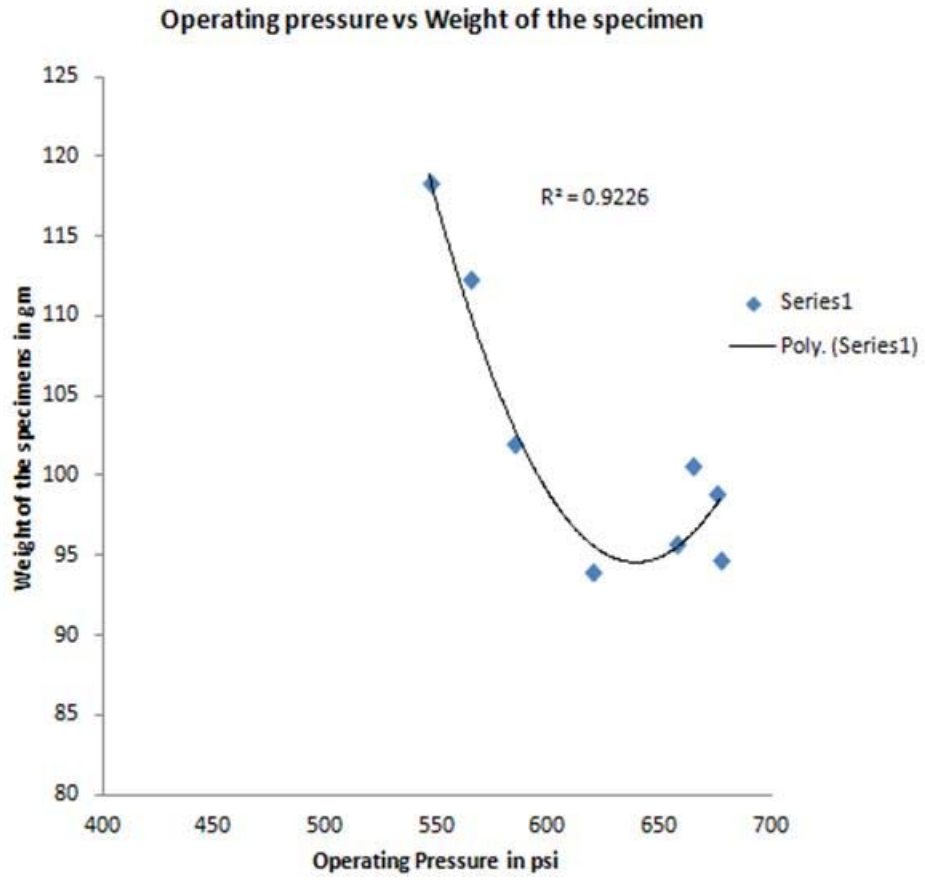


Figure 4.2 Graph showing relationship between P_2 and M_0

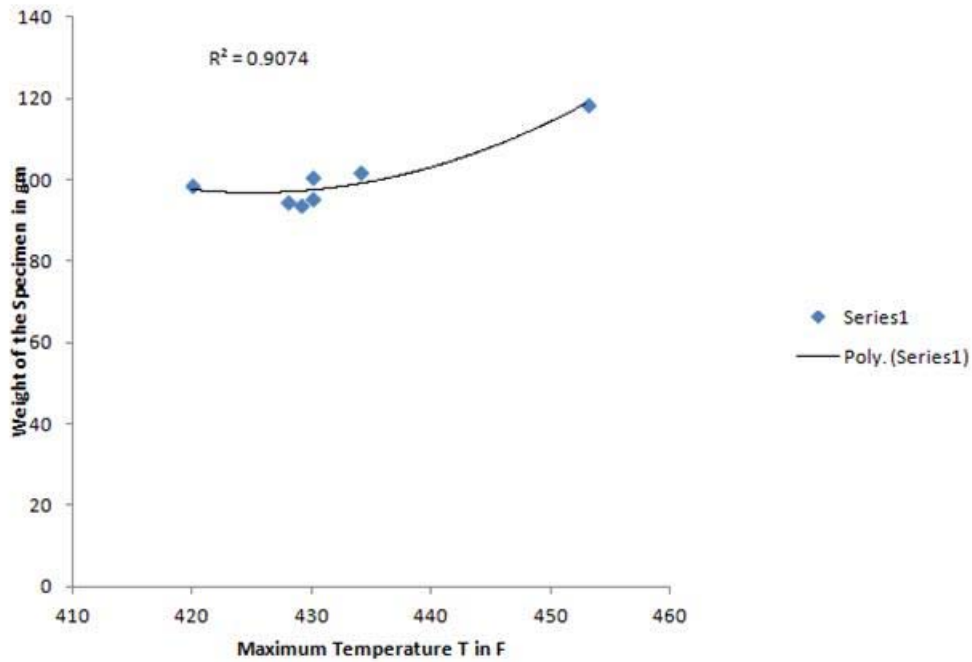


Figure 4.3 Graph showing relationship between T and M₀

4.1.1 Finding the sweet spot

The relationships between the operating parameters and the specimen weight were evaluated in the earlier section. This paves way for the calculation of the ideal configuration for making the specimens. Therefore, the briquetting process should be optimized to reduce the load on the hydraulic press and the energy consumed by the heaters. This can be done by finding the *sweet spot*, i.e. a situation in which the briquetting process can be run at low operating pressures and temperatures.

This can be done by drawing an X-Y scatter chart in which the specimen weight is taken as the independent variable and both pressure and temperature as the dependent

variables and the maximum specimen weight is evaluated at the least pressure and temperature conditions.

Assuming that the quantity of the material to be constant, the most ideal configuration as indicated in Figure 4.4, lies between the first and second specimens from table 4.3. This means that if the operating temperature and pressures of the process are maintained between the values indicated by specimen 1 and 2, high density specimens can be obtained.

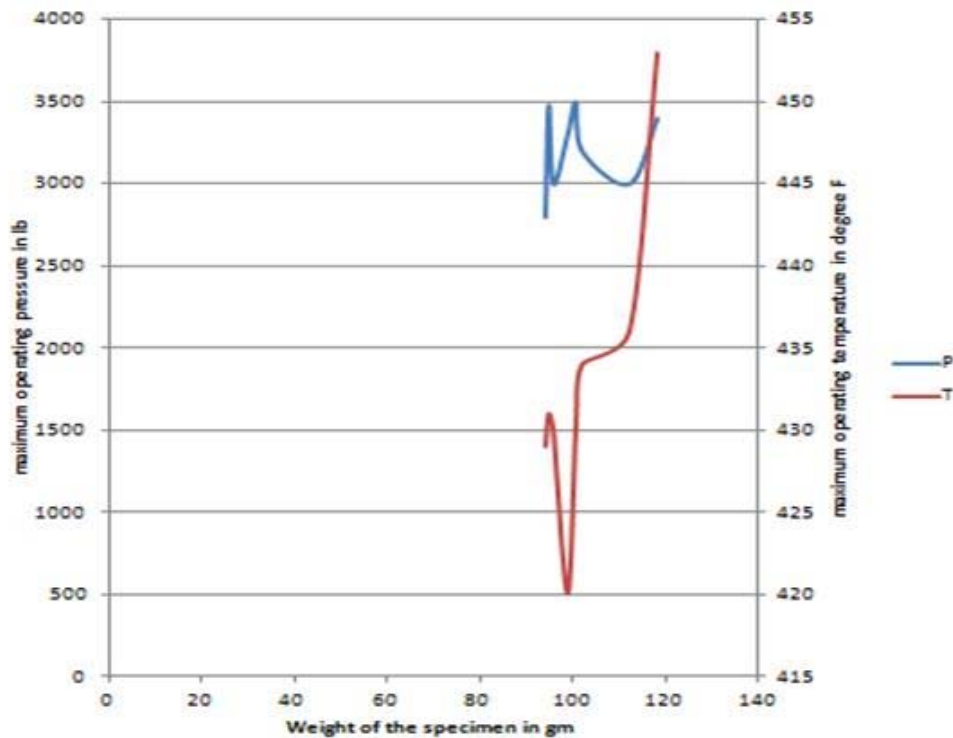


Figure 4.4 graph representing the sweet spot

4.2 Results of Carbonization

The green briquettes are subjected to carbonization in a furnace at 1100°C for about 6 hours in a Nitrogen atmosphere. The specimens after carbonization are removed for observation. It is discovered that there has been a significant amount of weight loss due to the depolymerization and the resultant mass is a highly porous and carbonaceous solid. The specimens are weighed upon removal from the furnace to evaluate the weight loss. The following table shows describes the weight of the coked specimens along with their dimensions. Figure 4.5 describes the results of the carbonization.

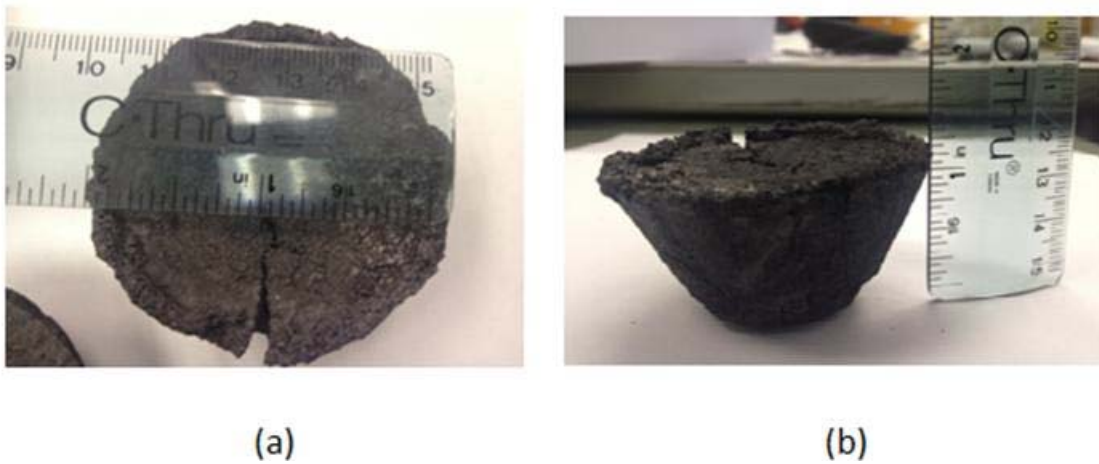


Figure 4.5 Specimen diameter and length after carbonization at 1100°C for 6 hours

Table 4.4 Coked specimens obtained from green briquettes from table 4.1 and one specimen from 4.2

Sample No.	Mass of the coked specimen, M (gm)	Height of the coked specimen, H (inches)	Outer diameter, D1 (inches)	Inner diameter, D2 (inches)
1	32.7	1.23	1.9	1.3
2	26.2	1.1	2.0	1.2
3	31	1.15	2.0	1.2
4	34.5	1.3	2.2	1.2
5	31.4	1.3	2.0	1.2
6	26.9	1.15	2.0	1.2
7	28.4	1.2	2.1	1.2
8	33.4	1.3	2.1	1.2
9	28.3	1.2	2.1	1.2
10	24	1.1	2.0	1.2
11	22.5	1.0	1.9	1.5
12	25.9	1.2	1.9	1.1
13	29.5	1.3	2.0	1.2

4.3 Results of the volatility test

As observed from the tables, a mass reduction of about 66% has occurred after the carbonization process. The green briquettes produced prior to the change in the feeding process i.e. the specimens discussed in Table 4.2 were carbonized in the furnace. The total weight of the specimens was around 721 gm. These specimens were carbonized in the furnace for 3 hours at 1100°C by incrementing the temperature by 200°C every hour. The Specimens extracted from the furnace for tested for volatiles after a few days.

A total of 11 specimens weighing 238.6 gm were considered for the test. The specimens were weighed at room temperature before being placed in the furnace. The specimens were then heated to 100°C and were removed to measure the weight again. This time, the weight of the specimens was found to be 232 gm. The specimens were again transferred into the furnace, to be heated at 1100°C for 3 hours in a Nitrogen atmosphere. This was achieved by incrementing the temperature by 200°C every hour.

After letting the specimens dwell at 1100°C for 3 hours, they were cooled down to 100°C at which point they were weighed again. Now, the mass of the specimens was found to be 211.4 gm. Since a mass reduction of about 11% had occurred, the process was repeated. This time, the weight of the specimens was 209 gm. Since the mass reduction was very low this time, it was concluded that the percentage of volatiles present in biocoke specimens was less.

The coke specimens referred in Table 4.4 were carbonized noting the affects of the volatility test. Taking the results of the volatility test into consideration, the dwelling time for the carbonization was changed to 6 hours. This would account for the elimination of excess volatiles.

4.4 Biochar: discussion



Figure 4.6 Bio char green briquettes

After multiple attempts to prepare green briquettes from biochar, it was found that the process did not apply for it. Apparently, the binder could not adhere to the biochar resulting in weak, porous and broken specimens. Also, this may be due to the fact that bio oil and biochar are the products of the fast pyrolysis process. Since these are separated after the process, it may be unlikely that they would recombine.

4.5 Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) testing

The samples of biocoke weighing 650 gm were sent to the labs of ArcelorMittal [1] for the *CRI/CSR* testing. A customized version of the reactivity test was done. The test involved the usage of 50 gm of the material as the sample, which was crushed using a 18 by 40 mesh sample size to determine the reactivity. The crushed sample was then heated in a blast furnace first in the presence of nitrogen and then in the presence of CO₂ (the flow rate was unspecified) at 1825°F for about 120 minutes. This test however, did not include the tumble test done after being removed from the furnace to determine the *CSR*. Duplicate analyses using the same sample size and operating conditions were run for confirmation of the test results.

The results of the coke reactivity test were then sent from the test facility. It was observed that two samples were prepared from the specimens, each weighing 50 gm and the test was run under the conditions specified above. As part of the reactivity test, the percentage of volatiles were also measured. Table 4.5 illustrates the results of the reactivity test performed on the two samples as described above.

The percentage of reacted coke for the first sample was 21.08 with 7.78 percentage of volatile matter. The second sample the percentage of reacted coke was 26.52. however, the sample size was not sufficient to compute the percentage of volatility.

Table 4.5 Reactivity test on two samples obtained from the coke specimens

Sample ID (lab code) coke-VM	% Reacted Coke	% Volatile Materials	% Reactivity (of Reacted coke)
#1 R&D (B00148)	21.08	7.78	13.30
#2 R&D (B00149)	26.52	--	--

4.6 References cited

- [1] "ArcelorMittal", retrieved from www.arcelormittal.com

CHAPTER V

CONCLUSIONS AND FUTURE WORK

The briquetting process was successfully carried out to produce green briquettes. The biocoke preparation process was developed right from mold design, raw material processing, the determination of the process parameters , briquetting and finally carbonization. Basic physical testing like the density test and the drop test were done on the green briquettes. To validate the chemical and physical properties of the specimens, a number of tests can be performed on the biocoke viz. the ASTM [1] standard ash test, sulfur test, heating value test and the volatile test.

To determine the behavior of the biocoke in a blast furnace, the blast furnace conditions are simulated in the CRI/CSR tests [1]. The specimens described in this process were originally prepared for the aforementioned testing process, which is being conducted by an external agency. The results of the tests are important because they will decide the direction the research will take. The blast furnaces require the value of the CSR to be greater than 60 and the value of the CRI to be lesser than 25 0. If the results of the CSR/CRI tests on the biocoke specimens are within the confined standards, research can be focused on the automation of the process, setting up a pilot plant for continuous production etc.

Since the results of the tests were favorable as discussed in the previous chapter, research can be focused on a new mold design to produce bigger and stronger specimens

and tweaking the "*recipe*" to produce better quality specimens, so that they can be tested again. However, if the results of the test are disappointing, then the potential of the research will be re-evaluated and then a decision will be made on the future of the research.

5.1 References cited:

- [1] ASTM D5341 - 99(2010)e1 Standard Test Method for Measuring Coke Reactivity Index (CRI) and Coke Strength After Reaction (CSR)
- [2] Diez, M., Alvarez, R., and Barriocanal, C., 2002, "Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking," International Journal of Coal Geology, 50(1), pp. 389-412.