Addis Ababa University,
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Liquid Fuel Production through Pyrolysis of Khat and Plastic Waste Mixture

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February 27, 2014

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of a Master's Degree in Chemical Engineering under Environmental Engineering

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ACRONYMS

ANOVA – Analysis of Variance

ASTM – American Society of Testing Materials

DF – Degree of Freedom

GHG – Greenhouse Gas

HDPE – High-Density Polyethylene

HHV – Higher Heating Value

LHV – Lower Heating Value

MSW – Municipal Solid Waste

OFAT – One-Factor-At-A-Time

RSM – Response Surface Method

SW – Solid Waste

SWM – Solid Waste Management

ABSTRACT

A good portion of the Ethiopian population, especially of the youth, has taken up the habit of chewing *Khat* (scientific name: *Catha edulis Forsk*). Growing use of the stimulant is obviously generating a huge amount of waste making the already-bad situation of solid waste management in Addis Ababa worse. On the other hand, the disposal of plastics is also affecting the environment negatively and in no less a degree. With the expected increase in the consumption of both items, the problem will certainly grow correspondingly especially given the trend that *khat* is almost always sold in plastic bags. This study investigated the potentials of *khat* waste to be mixed with high-density polyethylene (HDPE) for use as a raw material in pyrolysis to produce liquid fuel. The results showed that *khat* waste can be used in pyrolysis, solely and in a mixture with waste HDPE, to yield liquid fuel. A maximum of 26%.wt of liquid yield was achieved. Produced data on characteristics of *khat* waste that were not available until now showed that *khat* waste had 76.3% moisture (as discarded); 5.31% ash (dry basis); 59% cellulose; 31.7% lignin; 47.12% C; 6% H; 45.65% O; 1.23% N; HHV of 17.5 MJ/kg; and LHV of 12.6 MJ/kg. A dark brownish liquid that had smoky odor was produced from all runs. An average liquid yield of 15.57% was obtained while the minimum and maximum values were 3% and 26%, respectively. The experiment studied respective influences from varying amount of *khat* in feed; pyrolysis temperature; and total pyrolysis time. It was seen that pyrolyzing *khat* waste alone and in higher percentages gave better results. Lower amount of *khat* (30%) in the feed composition led to higher yield at 550^{O}C. However, pyrolysis at the remaining temperatures studied (650^{O}C and 750^{O}C) showed corresponding increase in yield with increasing amount of *khat* (70% and 100%). As respective decomposition of its lignocellulosic components took place at higher temperatures (> 300^{O}C for cellulose, and > 500^{O}C for lignin), more amount of *khat* in the feed led to increased amount of liquid yield. Variation in the total pyrolysis time between 30 and 60 min did not have any significant effect. Following the similarity between elemental composition of bio-oil from pyrolysis and the parent biomass, the HHV and LHV of liquid product were calculated to be 17.1 MJ/kg and 15.05 MJ/kg, respectively. In general, the expected enhancement in liquid yield from presence of plastic was not observed. In the study, pyrolysis of *khat* waste alone (0% HDPE) gave the maximum percentage yield for liquid product. However, it would not be plausible to conclude that addition of plastic does not bring any benefit at all – only percentage yields but not qualities of liquid produced with and without HDPE in the feed were compared.

To Abba, Mommy, Lily, and Momi. I owe you my every bit

1. BACKGROUND

According to Addis Ababa City Government, 0.4kg of solid waste is generated from each resident every day. This results in an immense annual generation of which 80% is collected by the city's solid waste management (SWM) system. Micro and small enterprises (MSE) do the primary collection of these wastes to receive volume-based payments at the rate of ETB 30 per m^3 from the municipality. This figure coupled with the expenditures for transport and disposal share a significant portion of the municipality's budget. There is also informal solid waste collection by street boys, private sector enterprises, scavengers at dump sites, and the "*koralés*[1]". The SWM by the municipality focuses mainly on collection, storage, transportation, and disposal of solid wastes. The reuse, recycling, and energy recovery practice is almost inexistent. Nonetheless, informal sector performs most of the collection of recyclable wastes which are to be used by local plastic, shoe, and metal factories. (Addis Ababa City Government, 2010)

Of the thousands of tons of solid wastes thrown out each year, plastics and biomass are among those which should be included in any waste management system. If not properly managed, disposal of these wastes is very harmful to public health causing high rate of pollution as it eventually makes land inhabitable by contaminating the soil. The overall awareness of the adverse environmental effects as well as the potential of plastics for energy recovery can be seen as promising at least around the different institutions in Addis Ababa and other cities and towns in Ethiopia. However, interventions to promote and/or introduce processing techniques to recover energy from plastics; and initiatives for efficient management of biomass through methods other than composting are undoubtedly at their infancy.

Leaves of *khat* are chewed for their stimulating effect by many people. Ethiopians that consume it daily are in millions (Lemessa, 2001). Waste from *khat*, known locally as "*Garaba*", seem to be hiking in an alarming rate to form a considerable portion of Addis Ababa's solid waste. It has caused, and still, remains to pose some major environmental risks. *Khat* waste can be seen in different parts of the city piled up along many side roads, in the vicinities of "*khat* shops", vacant and open areas, and in drains. Beside dirtying places, *khat* wastes are also capable of triggering respiratory and other diseases (Shimelis, 2011).

[1] *Koralé* – Refers to a vendors (commonly male) going around houses to collect scrap metals and other discarded materials that have market worth.

1.1 Statement of the Problem

Consumption of the plant *khat* (scientific name: *Catha edulis Forsk*) in Ethiopia has long since become one of the hallmarks of urban centers—old and new alike. A good portion of the population, especially among the youth, has taken up the habit of chewing it (despite the escalating price) so much so that trade in *khat* and delivery of associated services are growing fast and spreading far and wide. The ever widening use of the stimulant is obviously generating a huge amount of waste making the already-bad situation of solid waste management in Addis Ababa worse.

The lesser combustibility of *khat* waste has largely rendered it less preferable among low income groups to be included as a fire wood. This may explain why *khat* waste ends up in many street corners of Addis Ababa and in almost all the other urban centers to be swept into sewerage lines.

On the other hand, plastics have become so omnipresent and their use so varied that it may be hard to imagine how life was, and will be, managed without them. The use of plastic materials permeates industrial products in auto mechanics, electronics, construction, fabrics, household utensils and cutleries, and innumerable varieties of packages, containers and wrappers. The popularity and indeed indispensability of plastics in household and industrial uses emanates from their lightness, simplicity, ease to utilize, affordability etc.

These amenities of plastic are, however, overshadowed by the problems associated with the large amount of waste they leave in their wake. The problem of plastic waste disposal is even more compounded by its non-biodegradability. The threat to environment posed by the absence and/or lack of proper plastic waste management has already become widely manifest to need any elaboration. Plastic waste clogs sewerage lines and is unable to decompose for hundreds of years and some forever affect perviousness which impacts drainage and soil fertility.

The use of plastics, as much as it has eased life in rural communities, is in no less a degree negatively affecting livestock that inadvertently feed on plastic material that litter grazing grounds.

The current problem in the management of plastic and *khat* waste is already posing a serious threat to the environment. With the expected increase in the consumption of both items, the problem will certainly grow correspondingly. Needless to say that this problem has to be somehow addressed; and addressed fast, before the damage on the environment gets

irreversible. It would so be agreeable that recovering energy from these wastes is a very good way of managing them.

The present research aims at studying the possibility of recovering energy from *khat*, and plastic (HDPE) waste by using their mixture in a pyrolysis process.

1.2 Objectives

1.2.1 General Objective

The general objective of the study was to investigate the potential for liquid fuel production from the mixture of khat and high-density polyethylene (HDPE) wastes through pyrolysis.

1.2.2 Specific Objectives

This study also had the following specific objectives:

- Characterize khat waste;
- Study the pyrolysis process of khat and high-density polyethylene(HDPE) waste mixture for the production of liquid fuel;
- Investigate the effect of process conditions on liquid product yield, and;
- Characterize liquid fuel.

1.3 Significance of the Study

This study, by investigating the possibility of using waste *khat* and plastic (HDPE) for energy recovery, will contribute to make available an alternative way of handling the wastes. As it is also the pioneer to characterize and process *khat* waste for a purpose as such, the findings can be used as a reference for future studies.

2. LITERATURE REVIEW

2.1 Municipal Solid Waste (MSW) Management in Addis Ababa

Waste generation rate of Addis Ababa was 0.4 kg/cap/day in 2010 which, according to the city administration, resulted in annual rate of more than 200,000 tons. Of this amount, 80% was collected by the city's solid waste management (SWM) system in which micro- and small-scale enterprises (MSE) did the primary collection of these wastes to receive volume-based payments at a rate of ETB 30 per m^3 from the municipality. Conceivably, this would make up a large proportion of the municipality's expenditure considering associated costs for transportation and disposal. The secondary stage of collection was, on the other hand, "represented" by several collectors such as street boys, private sector enterprises, scavengers at landfill and dump sites, and the *koralé* (Addis Ababa City Government, 2010). Furthermore, the municipality's concern, with regard to SWM, was mainly on collection, storage, transportation, and disposal without any roles in recycling and energy/material recovery. Whatever volume or amount of material recovery for recycling and/or reuse was effected, the credit goes to the informal sector which performed most of the collection of recyclable wastes which were to be used by local plastic, shoe, and metal factories.

SWM in urban areas around the world has all along remained a major concern of both the municipalities and the populace. It was, however, accorded with very minimal attention particularly in most of the developing countries which led to a substantial deterioration of the overall environmental management. It was only very recently that some hints of realization of the ramifications of poor and/or improper handling of solid wastes were observed in some low- and middle-income countries. Financing of SWM in such countries thus be of a big burden to the municipalities. Ethiopia, and hence its cities, are no exceptions in this regard (Shimelis, 2011).

Be it in developed or not so much developed cities perhaps the most prominent shortcoming is the threat posed by solid waste on the environment and public health. The health of the population in Ethiopian urban centers is endangered due to improper and uncontrolled disposal of solid waste hence dumping along roadsides and in open areas. SWM that are seen among respective municipalities and concerned bureaus in the country are, unfortunately, very poor (Tewodros, Arjan, & Fitsum, 2008).

Although the task began a long time ago, management of solid wastes in Addis Ababa has not been performing properly. The service had not been able to operate commensurate to the city's requirements in terms of both generated amounts and composition of waste. Residents, as a result, not only believe that MSW management did not function properly but it also led to their discomfort to cooperate and/or pay for on-site collection services (Nigatu Regassa et.al., 2011).

An entity at the *kebelé* (now officially known as *woreda*) level known as Cleaning and Beautification Department (CBD) was entrusted with the task of management of wastes in the city in 2008. However, tight budgets, absence of qualified personnel, and lack of experience in SWM prevailed in the CBD. This has led to its rather formidable struggle (Nigatu Regassa et.al., 2011).

Management of MSW components can be a complex problem since it involves a multitude of requirements in the spectra of science, technology, economics, and societal issues that have to be addresses. It is the unfulfilled elements among these factors that resulted in an improper management of MSW in Addis Ababa which in turn led to increased risks on the environment. (Nigatu Regassa et.al., 2011)

Biomass and plastic wastes are undoubtedly among those that require due attention and proper management because of the potential harms they can cause on the environment. Contribution to global warming due to the emission of GHGs; air pollutions caused by the release of various pollutants; ground water pollution because of leachates; and increased perviousness of land leading to land degradation are among the serious environmental threats that are posed by such solid wastes. Collection and disposal of solid wastes, however, is poorly operated in the city of Addis Ababa. Lack of proper management structure, and absence of facilities that could have ensured "functioning" MSW management system are the major causes (Nigatu Regassa et.al., 2011).

2.2 Pyrolysis of Solid Waste

Processing waste for the purpose of material and/or energy recovery can be carried out through many ways. Several distinct methods are available to deal with solid waste management ranging from simple systems – for proper disposal of SW – to complex ones – to achieve safe management of industrial and hazardous wastes.

Major solid waste conversion processes can be put under three categories: *thermochemical, biochemical,* and *physicochemical* each having the objective of converting solid waste

materials to energy (Costello, 2009). As their names indicate, these methods aim at exploiting, respectively, *thermal*, *biological*, and *physical* properties of solid waste materials.

In thermochemical conversion processes decomposition of organic matter occurs due to the heat supplied resulting in high temperatures throughout the waste material(s) being processed. The otherwise-discarded waste materials would then be valorized by this process producing heat energy, fuel oil, and/or combustible gas. Thermochemical conversion processes can be said to be useful, among others, primarily in the management of wastes containing high percentage of organic non-biodegradable matter, and low moisture content. Those processes which are characterized by higher temperatures and conversion rates especially suit well the processing of feedstock having lower moisture content that would have been generally considered as less selectable for products. Combustion, pyrolysis, gasification, and incineration are the main technological alternatives under thermochemical conversion processes. These processes are depicted in the figure below together with respective energy and material recovery systems. (Begum, Rasul, & Akbar, 2012).

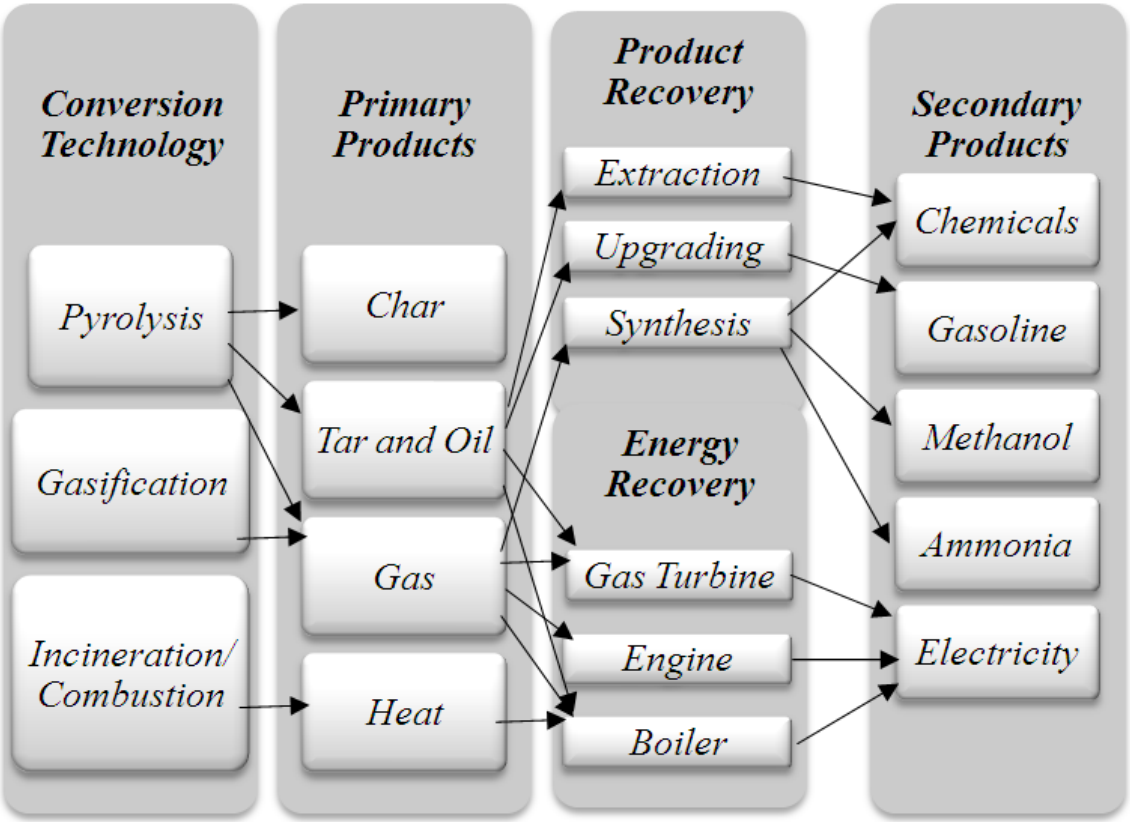


Figure 2-1 – Thermochemical Waste Conversion Processes
Source: (Begum et. al., 2012, p. 625)

Pyrolysis can be described as a process of chemical and thermal decomposition that generally leads to smaller molecules. Sometimes referred to as *Thermolysis*, pyrolysis (Greek: *pur* = fire; *luo* = loosen) provides for the disposal of solid wastes with recovery of valuable materials. Chemical decomposition of solid wastes, mostly organic, takes place in a heated and oxygen-deficient, or vacuum, atmosphere. Depending on the organic characteristic of the waste being processed, pyrolysis often results in a gas stream containing primarily hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), and various other gases and inert ash.

Decomposition of carbonaceous materials by using heat (thermal degradation) takes place in pyrolysis where typical temperatures can lie between 400 and 800^{O}C in an environment where there is no or limited oxygen. This endothermic process that produces pyrolytic oil and gas (syngas), and solid char, however, involves no direct heating. After the appropriate treatment that should follow, pyrolytic oils can be used for liquid fuels, chemicals, adhesives, and other products for several applications. Direct combustion of pyrolysis products – gases, oils, and char – is also possible in a number of processes. (Begum, Rasul, & Akbar, 2012) (Young, 2010)

It is typical of most organic compounds to be thermally unstable and to have chemical bonds of their molecules break at high temperatures producing smaller molecules such as hydrocarbon- and hydrogen gases. At high temperatures, the thermodynamically stable small molecules of CO and H_2 predominantly make up the gas mixture produced which is known as syngas.

Waste material is thus converted through pyrolysis into solid and volatile matter. Variously termed char, charcoal, or coke, the solid product is of high carbon content and may contain around half the total carbon of the original organic matter (Brownsort, 2009). A condensation step included in the pyrolysis process will give a liquid fraction from the volatiles which are partly condensed. A mixture of gases (non-condensable) will also evolve from the process.

Figure 2-2 below shows schematic representation of a typical pyrolysis process employed in the production of electricity from MSW. Preprocessing of the feedstock is included to first remove profitable recyclable components from the waste. The preprocessed material is then fed into the pyrolysis reactor that is heated indirectly to bring the contents' temperature between 650 and 1,200^{O}C. Raw syngas is finally produced overhead while ash, carbon char, and metals are bottom products.

Removal of carry-over particulate matter from the reactor, and other constituents (such as sulfur), chlorides and acid gases (such as hydrochloric acid), and trace metals (such as mercury) will be achieved in the syngas cleanup step. Syngas is used in the power generation plant to produce steam and electricity that will be used in the process and also distributed to consumers.

The bottoms of the reactor are ash, carbon char, and metals. While the latter two have uses as recyclables in industry, the ash is usually disposed of in a landfill. An environmental shortcoming of pyrolysis that is noteworthy when used for MSW management is this type of disposal of the ash from the process (Young, 2010).

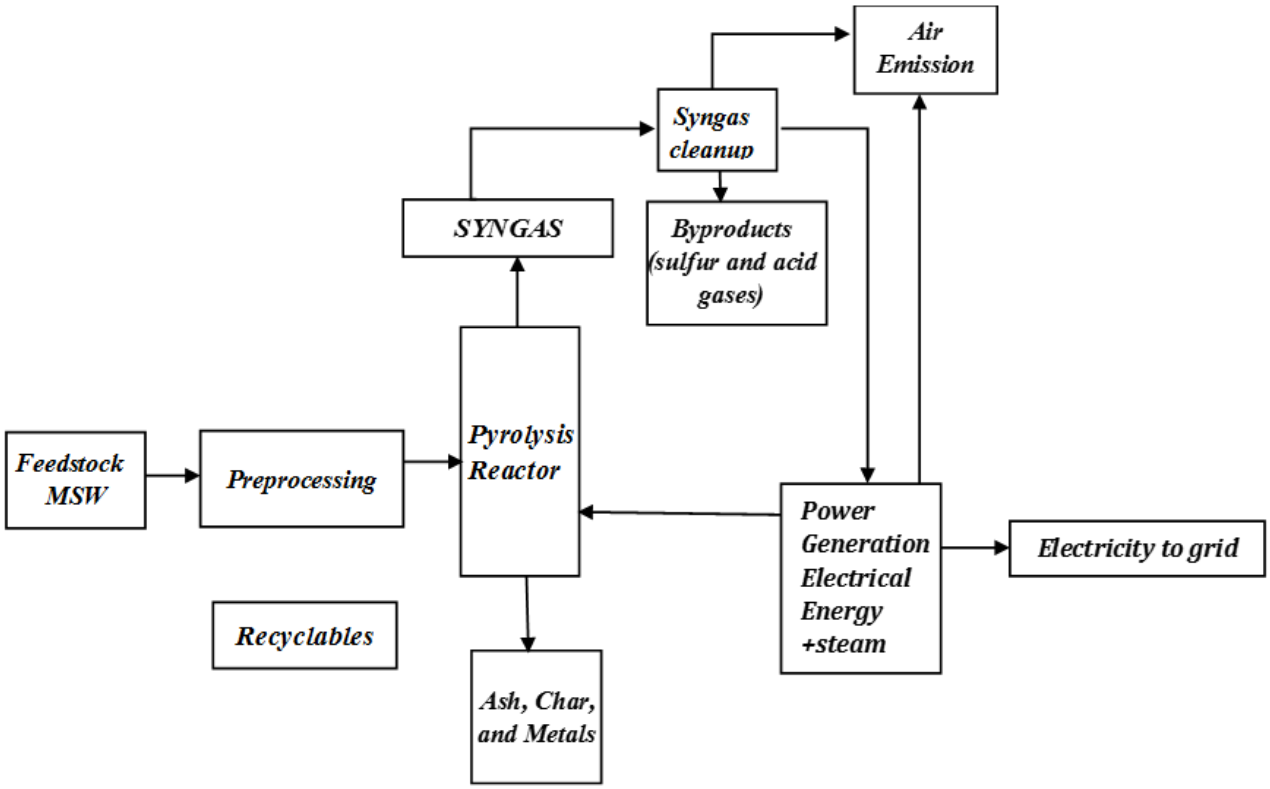


Figure 2-2 – Production of Electricity from MSW via Pyrolysis
Source: (Young, 2010, p. 5)

2.2.1 Applications of Pyrolysis

Application of pyrolysis for proper management of solid waste and resource recovery from a wide variety of feedstock is its main allure. Solid waste materials that are otherwise difficult to safely dispose can thus be used as feedstock for pyrolysis to end up as useable products for numerous applications. Tire wastes, coal and petroleum residues, used lubricating (or heavy) oils, sewage sludge, and contaminated soil are only some of the materials that can be pyrolyzed.

Tire recycling, energy recovery from sewage sludge, and soil cleaning can hence be achieved (Riediger & Gerlach, 2010). Brief discussions of these applications are given below.

Tire Recycling: Pyrolysis of end-of-life tires gives high energy gas, hydrocarbon oils, char, and steel. This can be attributed to the presence of a lot of chemical bound energy. The high energy gas produced may be utilized as a source of energy for the pyrolysis process while the pyrolytic oil may be used as a fuel independently or mixed with diesel fuel in different ratios. After additional processing, the char may be used as a carbon black substitute or precursor of carbon adsorbents.

Sewage Sludge: Efficiency of sludge pyrolysis is very often discussed in many literatures. Pyrolysis of sludge is a very energy-efficient process and the dryer the sludge the more energy efficient the main process. A more energy efficient process can also be achieved through the usage of undigested sludge for nearly double the energy content is found than that of digested sludge from the biogas plants.

Soil Cleaning: Soil which is contaminated with oil, hydrocarbons, dioxins, furans, or mercury can be purified by pyrolysis. For this application raised temperatures can be reached by using either direct or indirect heated kilns. Heating converts the volatiles to vapor which is incinerated in a downstream combustion chamber. While requiring more expensive costs for heating devices, indirect heated kiln, compared to a direct heated one, produces much less process gas which minimizes the flue gas cleaning process.

2.2.2 Pyrolysis vs. other Thermochemical Waste Conversion Methods

Inclination towards the use of pyrolysis technology is increasing favoring it for being the most appropriate and an economically feasible approach for the management of solid wastes. Residential, commercial, industrial, and MSWs as well as a mixture of these wastes can be valorized, hence properly managed, by employing this technique (Young, 2010).

As one of the several options to recover energy from solid waste, pyrolysis offers additional benefits. Preference of pyrolysis over other methods may come due to its relative simplicity, its adaptability to process a wide range of feedstock, and its ability to achieve the production of many products of high value from different types of solid waste. Advantages of pyrolysis as compared to other thermochemical processes include:

1. It is applicable for all types of solid waste, and it ensures easy adaptability to changing composition in the feedstock;
2. It can be conducted as a batch, low pressure process with minimal requirements for feedstock preprocessing;
3. Production of several valuable products from different solid wastes for wide range of applications is realized through pyrolysis which include CO_2, CO, H_2O, H_2, NH_3, CH_4, etc…;
4. Design of the technology can be made to allow production of minimal amounts of unusable by-products;
5. Significant reduction of the storage volume required for waste materials is achieved while efficient storage of important elements such as carbon and nitrogen is allowed in the form of pyrolysis char and later recovered by gasification or incineration when needed.
6. It employs simple technology which can be made compact and lightweight. It is even among the several options for solid waste resource recovery in space. It has the advantage of being adaptable to a wide variety of feedstock to produce several usable products from typical solid waste streams from spacecraft operation (Serio et al., 2002).

A summary of the thermochemical conversion processes in terms of respective advantages and disadvantages can be found in (Begum et. al., 2012, p. 629)

2.3 Biomass

Any living matter on earth is a source for biomass. Biomass feedstock can be categorized into three – wastes, forest residues, and crops. Wastes refer to biomass residues mostly from agricultural and MSW while forest residues include saw dust, wood and bark residues, and crops are such as those from short rotation, sugar cane bagasse, oil seed, grasses and cereals (Danje, 2011).

Biomass fuels work by releasing solar energy. Plants, for instance, undergo photosynthesis to produce biomass. Through photosynthesis, they convert solar energy to chemical energy, which fuels plant growth. Human beings, in turn, use this stored solar energy through fuels such as wood, alcohol, and methane that are extracted from the plant life – biomass.

2.3.1 Constituents of Biomass

Constituents of biomass differ with varying types and species of the biomass with their chemical components being very different from those of the fossil fuels (Mohan, et al., 2006).

Oxygen-containing organic polymers prevail in plant biomass which makes them essentially a composite material constructed from these chemical compounds. The major components of plant biomass as shown in the figure below.

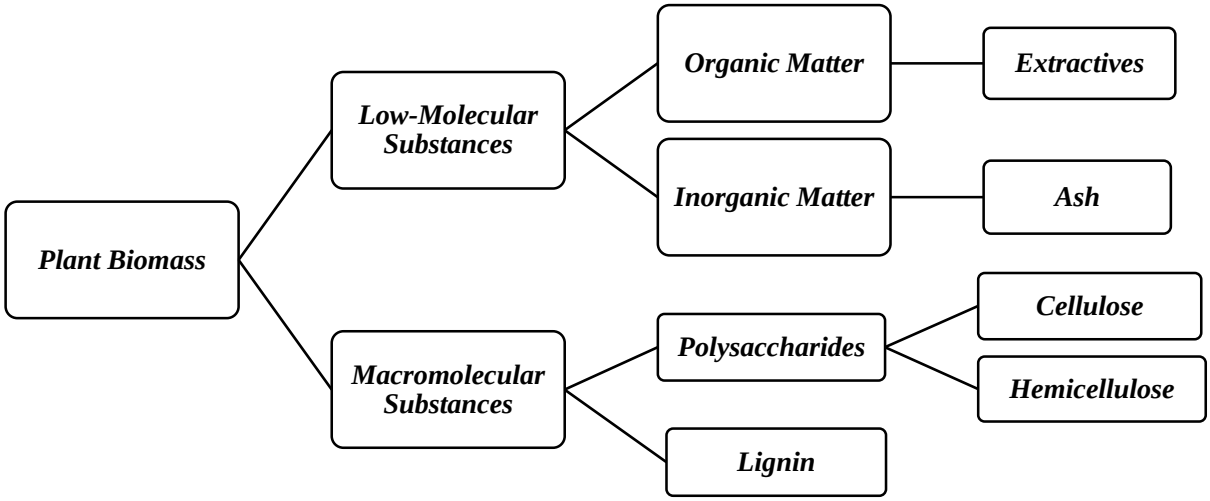


Figure 2-3 – General Components in Plant Biomass
Source: (Danje, 2011, p. 7)

Complex mixture of numerous compounds make up plant biomass among which lignin, cellulose and hemicellulose are the major ones. These components, also known collectively as *lignocellulosic* composition of biomass, are present with their varying ratios and properties as per the type (species) of the plant. Compositions of different types of biomass in terms of the respective weight-percentages are shown in the table below.

Table 2-1– Composition of Different Biomass Types
Source - (Danje, 2011)

TYPE	**COMPOSITION (wt% on dry basis)**			
	Cellulose	***Hemicellulose***	***Lignin***	***Ash***
Soft Wood	41	24	28	0.4
Hard Wood	39	35	20	0.3
Pine Bark	34	16	34	2
Wheat Straw	40	28	17	7
Rice Husks	40	25	12	16
Peat	10	32	44	6

2.3.1.1 Cellulose

Cellulose (Latin *cellula*, "little cell") is a complex carbohydrate compound which is the principal constituent of cell wall. It is the most abundant organic compound on the planet and its treatment with chemicals produces a number of useful substances, including starch for coating parchment paper, and the threads and film that form rayon and cellophane. Pine, for example, can be utilized for its cellulose which can be used in the manufacture of textiles (Vigouroux, 2001).

A cellulose molecule is made up of linear chains of 1,4-D-glucopyranose units (Figure 2-4). The units are linked 1–4 in the alpha-configuration (Pinthong, 2009). It has an average molecular weight of around 10^6 Da or above (Mohan, et al., 2006).

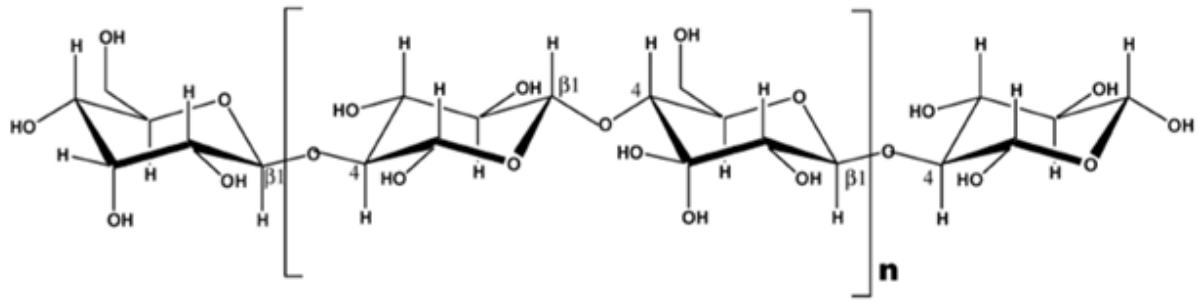


Figure 2-4 – Chemical Structure of Cellulose
Source: (Mohan, et al., 2006)

The intra-molecular and intermolecular hydrogen bonds contained in the molecule give cellulose crystals which make it completely insoluble in aqueous solutions and soluble in solvents such as *N*-methylmorpholine-*N*-oxide (NMNO), CdO/ethylenediamine (cadoxen) and dimethylacetamide. In most biomass, cellulose takes the largest portion of lignocellulosic components followed by hemicelluloses, lignin and ash (Sinha, et al., 2004).

2.3.1.2 Hemicellulose

The presence of branched structures in a biomass is mostly attributed to the existence of hemicellulose. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methylglucoronic and galaturonic acids, with an average molecular weight of 30,000 Da (Pinthong, 2009); (Danje, 2011)

2.3.1.3 Lignin

The other important constituents of many cell walls are *lignins*, which add rigidity to plants. *Lignin* is a complex chemical compound and one of the most abundant organic polymers. It

forms 30% of non-fossil organic carbon and constitutes from 25% to 33% of the dry mass of wood.

Lignin is an integral part of the secondary cell walls of plants and some algae. In the chemical context, it refers to aromatic polymers (existing in certain biomass) which are characterized by being highly branched, substituted, and mononuclear. It is often found adjacent to cellulose fibers to form a ligno-cellulosic complex (Czernik, 2002). Lignin is, further, regarded as a group of chemically related compounds that are amorphous, and of high molecular weights. A three-carbon chain attached to rings of six carbon atoms, called phenyl-propanes, is believed to make up the major building blocks of lignin.

The removal of hydroxyl groups from sugars forms lignin. Through this phenomenon can alternatively be described by the creation of phenolic compounds and short-chain alcohol ligands which are also heavily cross-linked. According to (Mayhead, 2010) the basic monomer of lignin can also be thought of as 4-alkylcatechol. The alkyl ligand is a 1 to 3 carbon chain which may be substituted with hydroxy or keto ligands at any or all positions. Both phenol groups and the alkyl substitutions may cross-link to other monomers or their side chains, yielding a fairly light, but strongly cross-linked and randomly ordered mass, i.e., wood.

2.3.2 Waste Biomass Feedstock for this Research: Khat (*Catha edulis Forsk)*

Biomass wastes can be processed to recover organic content in a useful form which otherwise may pose a risk of fueling forest and other types of fires (Paradela, Pinto, Gulyurtlu, Cabrita, & Lapa, 2008). Pollution risks that can also arise from these wastes may also be minimized if duly processed to recover the organic content. CO_2 can be potentially emitted from such wastes that are exposed in open lots and/or other incineration activities carried out in an attempt to utilize or manage the wastes. The process of energy recovery to produce fuel from biomass wastes can hence hinder the contributions of these phenomena for the already-worsening condition and effects of climate change.

The biomass component of the feedstock that was used in this research was *khat* waste. *Khat* (*Catha edulis Forsk*) is an evergreen plant that is grown mainly in East Africa and some regions of Yemen. People consume *khat* for the stimulating effect it has which are similar to those of amphetamine. When chewed, the effects from the drug contained in the fresh leaves are felt as the result of their actions on the central nervous system (i.e. the brain and the spinal cord). People consuming *khat* would, therefore, get into psychological state(s) which they often

describe as pleasant and relaxing. Increased alertness and concentration, reduced fatigue, and concurrent rises of heart rate and blood pressure are some of the common ones indicated (WHO, 2006).

The plant is a shrub commonly 2–3 m in height but it can also be found to grow up to 7 m in height in equatorial regions. *Khat* tree, however, can grow as high as ≈ 5 m and 15–25 m when cultivated in the arid and equatorial regions, respectively (Paris, 1958) (Lemessa, 2001). Distribution area of this plant extends from South and Eastern Africa to Arabia and Afghanistan with Ethiopia, Somalia, and Yemen being the forefront sources. According to Paris, this plant was first mentioned in foreign sceintific literature by a Swedish man named Forsskal – a botanist and also the explorer of Lower Egypt and Arabia – who was also the one to initially call it *gat* or *khat*. The description of the plant came from his work which was included in *Flora aegyptico-arabica* which was published in 1775 after his death (Paris, 1958).

Narcotics in *khat*, in the vein of amphetamines, act by stimulating the release of *neurotransmitters* such as *norepinephrine* that result in increased brain activity, and raised heart rate and blood pressure. Senses of well-being, increased competence, and alertness are the primary as well as initial effects produced. Consumption in high dosage can cause tremors, sweating, heart palpitations, or anxiety. When the effects wear off, exhaustion, and/or perhaps depression follow. Prolonged use may, on some individuals, cause serious mental illness including paranoia, delusions, and hallucinations. Other chronic effects vis-à-vis psychological instability and disintegration may occur with high probability for cantankerousness and violent behavior to occur as well (WHO, 2006) (Nencini & Ahmed, 1989) .

Legend also has it that the use of *khat* was first discovered by a herder who noticed the effect of the plant on his goats and who tried it and experienced wakefulness and added strength. As some folktales have it, *khat* originated in Yemen, however recorded sources indicate that it originated in Ethiopia, specifically in Hararghe with a gradual expansion to different parts of Ethiopia, Yemen and other parts of the world (Lemessa, 2001).

2.3.2.1 Chemistry of Khat

Khat[1] refers to the leaves and the young shoots of the plant *Catha edulis Forsk* – a species in the Celastraceae plant family. Chemical profile of *khat* and thus its types are determined by the environment and climate conditions. Its taste varies from one kind to another and depends on the tannic acid content.

Many different compounds are found in *khat* including *alkaloids, terpenoids, flavonoids, sterols, glycosides, tannins, amino acids, vitamins* and *minerals*. The content of tannic acid *(average mol. formula $C_{14}H_{14}O_{11}$)* is what the taste of *khat* emanates from. However, *khat* leaves generally have an astringent taste – described as sharp and acidic – and an aromatic odor (WHO, 2006) (Cox & Rampes, 2003) (Kalix & Braenden, 1985) (Nencini & Ahmed, 1989). The young leaves are slightly sweet.

The phenylalkylamines and the cathedulins are the major alkaloids. The cathedulins are based on a poly-hydroxylated sesquiterpene skeleton and are basically polyesters of euonyminol. Only several years ago, 62 different cathedulins from fresh *khat* leaves were characterized (WHO, 2006).

The *khat* phenylalkylamines comprise cathinone [S-(–)-cathinone], and the two diastereoisomers cathine [1S,2S-(+)-norpseudoephedrine or (+)-norpseudoephedrine] and norephedrine [1R,2S- (–)-norephedrine]. These compounds are structurally related to amphetamine and noradrenaline. The plant contains the (–)-enantiomer of cathinone only; the (+)-enantiomer is not found. Thus, the naturally occurring S-(–)-cathinone has the same absolute configuration as S-(+)-amphetamine. Some basic descriptions of these phenylalkylamines and their chemical structures are given in

Table **2-2**, and Figure 2-5 and Figure 2-6 below, respectively.

Table 2-2 – Phenylalkylamines in Khat (*Catha edulis Forsk*)
Source: (WHO, 2006)

PHENYLALKYLAMINE	CHEMICAL NAMES	STEREOISOMERS (refers to)
Cathinone $C_9H_{11}NO$ (149.2 $g.mol^{-1}$)	• S-(–)-cathinone; • S-(–)-α-aminopropiophenone;	Naturally occurring S-(–)-cathinone;

[1] Other spellings of *khat* include *qat*, and *tschat.* While it is also called *"Jima"* in some parts of Ethiopia, it is known as "*miraa"* in Kenya). The dried leaves of *khat* are also known as *Abyssinian tea* or *Arabian tea* (WHO, 2006)

PHENYLALKYLAMINE	CHEMICAL NAMES	STEREOISOMERS (refers to)
	• (S)-2-amino-1-phenyl-1-propanone;	
Cathine $C_9H_{13}NO$ (151.2 $g.mol^{-1}$)	• 1S,2S-(+)-norpseudoephedrine; • 1S,2S-(+)- phenylpropanolamine; • 2-amino-1-phenyl-1-propanol;	Naturally occurring 1S,2S-(+)-norpseudoephedrine
Norephedrine $C_9H_{13}NO$ (151.2 $g.mol^{-1}$)	• 1R,2S-(–)-norephedrine; • 1R,2S-(–)- phenylpropanolamine; • 2-amino-1-phenyl-1-propanol;	Naturally occurring 1R,2S-(–)-norephedrine.

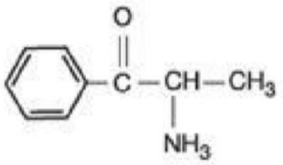


Figure 2-5 – Chemical Structure of Cathinone
Source: (WHO, 2006)

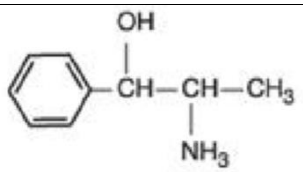


Figure 2-6 – Chemical Structure of Cathine, and Norephedrine
Source: (WHO, 2006)

Cathinone is the main psychoactive component of *khat* and it is unstable and undergoes decomposition reactions after harvesting and during drying or extraction of the plant material. This explains why fresh leaves are preferred and why *khat* is wrapped up in banana leaves to preserve freshness (WHO, 2006).

However, a very recent study by Atlabachew and colleagues has shown that it is possible to preserve *khat* samples for longer durations after freeze drying or deep freezing without significant loss of cathinone (Atlabachew, et al., 2013, p. 357). In their conclusion, it was indicated that it was wrong to assume that sun drying the leaves can result in complete decomposition of cathinone. More than 73% of cathinone was able to be preserved through refrigeration of samples after freeze drying or deep freezing.

2.3.2.2 Composition of Khat

The phenylalkylamine content of *khat* leaves varies within wide limits/ranges. Fresh *khat* of different origins contained on the average 36 mg cathinone, 120 mg cathine, and 8 mg norephedrine per 100 gram of leaves. The alkaloid content has been found to be higher in

Ethiopian and Tanzanian varieties than those grown in other countries which is why the former varieties are preferred (WHO, 2006).

A study by Darby and colleagues revealed that fresh leaf and tender twigs of *khat* can contain and contribute an important amount of nutrients to the diet (Lemessa, 2001). In a prior study, moreover, the contents given in Table 2-3 below were reported per 100 gm of fresh consumable parts. (Paris, 1958).

Table 2-3 – Composition of Khat
Source: (Paris, 1958)

ITEM	***AMOUNT***
Ash	1.6 gm
Protein (Nx6.25)	5.2 gm
Fiber	2.7 gm
Ascorbic Acid	161.0 mg
Thiamin	< 0.05 mg
Niacin	14.8 mg
Riboflavin	< 0.05 mg
Beta-carotene	1.8 mg
Calcium	18.5 mg
Iron	290 mg

2.3.2.3 Khat: The Ethiopian Context

A. Area and Production

Despite the official discouragement, and loud admonition of its consumers, not only is *khat* consumption expanding wide and fast it has long since become one of the most important cash crops in Ethiopia. There are strong domestic markets and as well in neighboring countries of Somalia, Djibouti, Yemen, and the Gulf States (Lemessa, 2001).

Greater number of farmers were and still are engaged in growing and producing stimulant crops such as *khat* and coffee than those growing fruits. The area and production of these crops were also larger than that of fruits since holders earned a considerable amount of money (CSA, 2006-2010). Table 2-4 below shows the amount of *khat* produced in Ethiopia along with respective percentage shares of the area under all crops in the country.

A 75% increase was seen in the amount of *khat* produced in 2010 than that of 2009. It can be inferred from this that the amount of *khat* waste generated – both during pre-processing for market and consumption – would also increase.

Table 2-4 – Area and Production of Khat in Ethiopia
Source: (CSA, 2006-2010)

PERIOD ***(Ethiopian Calendar)***	**AMOUNT OF KHAT PRODUCED (Million Quintals)**	**PERCENT OF AREA UNDER ALL CROP PRODUCTION (%)**
SEP 2005 – DEC 2006 (1999 E.C.)	*1.5*	*1.3*
SEP 2006 – DEC 2007 (2000 E.C.)	*1.3*	*1.37*
SEP 2007 –DEC 2008 (2001 E.C.)	*1.14*	*1.11*
SEP 2008 – DEC 2009 (2002 E.C.)	*1.16*	*1.08*
SEP 2009 – DEC 2010 (2003 E.C.)	*2.03*	*1.54*

The figures in the table above, the estimated percentage of *khat* that is marketed, and its perishable nature could altogether be used to extrapolate the enormous amount of waste generated. The spoiled aesthetics of roadsides and open spaces in Addis Ababa can be used to explain this phenomenon

B. Waste Generation Rate

The harvestable part of *khat* has consumable and non-consumable portions. The chewable portion is succulent and tender while leathery part is unfit for consumption. Based on the growth stage of the shoots and proportion of chewable parts, local people (farmers, traders and consumers) identify the variety of *khat* (types/kinds, and/or grades). In Ethiopia it is estimated that 85 to 90% of *khat* produce by farmers is sold while the rest is used for their own consumption in the household (Lemessa, 2001).

Khat has always been considered as a perishable commodity once it is harvested. There is no affordable means of storing it for a longer period of time other than the local and traditional way of sprinkling water and wrapping it airtight with banana leaves or transparent plastic sheets. Hence, it can be deduced that harvesting of *khat* certainly results in the generation of waste whether it is consumed or not.

Regardless of their respective amount, the management of *khat* and plastic wastes deserves good attention indubitably.

2.4 Plastics

Plastic commonly refers to materials that are made up of large and carbon-containing molecules. Numerous products can be formed from these compounds which may have several

uses. These products' properties, especially the useful ones, are given to plastics from the long carbon chain molecules that compose them. "Plastics can [thus] be made hard as stone, strong as steel, transparent as glass, light as wood, and elastic as rubber. More than 50 families of plastics have been produced, and new types are currently under development" (Richardson, 2006).

Plastics are also called polymers which are long and chainlike molecules. The repetition of a simple unit – the monomer – makes up the polymer molecule. Polystyrene is also known as "Styrofoam™" which is commonly found in electronic packing cartons. Its structure is depicted as either of the chemical structures below that show the whole polymer or simply the monomer with subscript, respectively.

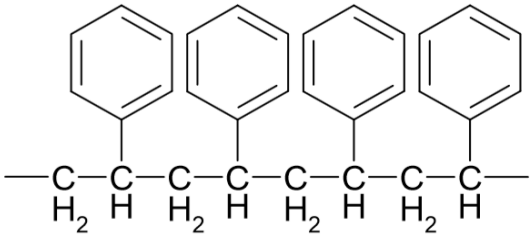


Figure 2-7 – Common Representation of PS Molecule
Source: (Gao, 2010)

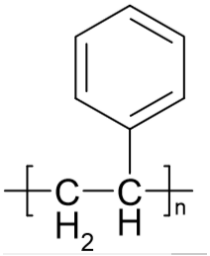


Figure 2-8 – Simplified Representation of PS
Source: (Gao, 2010)

There are many properties of plastics that make them and their application very useful in a wide range of varieties. It is relatively inexpensive to produce plastics which are lighter than many materials of comparable strength. Unlike the adverse effects brought about by the properties of wood and metals, plastics provide the benefit of not rusting or rotting. Any color of choice can be taken to manufacture plastics which can, moreover, be made as transparent, translucent, or opaque as needed.

Nevertheless, plastics also have some cons that can limit their selection for processing or restricts the spectrum of their application for some purposes. Some of the important properties

that are offered by plastics along with some of their major disadvantages are listed below (Richardson, 2006):

- Plastics are lighter due to their lower density than that of metals;
    - Most plastics vary in density from 0.9 to 2.2 g/cm^3,
- It is possible to reinforce plastics with glass and other fibers to form materials that are incredibly strong.
    - For example, nylon reinforced with glass can have a tensile strength of up to 165 MPa.
- Plastics are, in general, not the materials of choice if and when high heat resistance is needed.
    - This is attributed mainly because they are very thermally unstable. However, there are some plastic materials which are specifically designed to withstand temperatures as high as $288^{O}C$.
- Incineration or burning of some plastics produces poisonous fumes.
- Because of their molecular stability, plastics do not easily break down into simpler components which also means that plastics do not easily degrade or decompose on their own.
    - Plastics are thus regarded among the many, if not primary, materials that are "non-biodegradable" which pose extremely high pollution threats on our environment.

This lack of biodegradability inhibits the decomposition of plastics without the need for additional processing. As a result, plastics are one of the major environmental nuisances the disposal and/or management of which involves a great complexity.

Chemical structure, synthesis process, density, and other properties of plastic can be used to classify this ubiquitous commodity per se. The categorization can have different goals which may aim at providing a sort of simplicity in one or more of the activities that are involved in the general handling of plastics – be it by consumers and/or manufacturers. For instance, Society of Plastic Industry (SPI) defined a resin identification code system to assist in their sorting and hence recycling. This system divides plastics into the following seven groups based on the chemical structure and applications (Gao, 2010):

1. Polyethylene Terephthalate (PET);
2. High Density Polyethylene (HDPE);
3. Polyvinyl Chloride (PVC);
4. Low Density Polyethylene (LDPE);
5. Polypropylene (PP);
6. Polystyrene (PS), and;
7. Others.

This classification is used to distinguish between common plastic commodities through the corresponding numbers printed or engraved on plastic materials (like water bottles and packing). The symbol is formed by enclosing the number within a triangle made by rotating arrows that signify that the material is recyclable (Figure 2-9).

Figure 2-9 – Numbered Symbols of the Seven Types of Plastics
Source: (Gao, 2010)

2.5 Pyrolysis of Biomass

When put through pyrolysis, biomass feedstock decompose in a thermo-chemical way. Heating up of the biomass to a certain desired temperature in an inert (N_2) atmosphere where oxygen is also absent or present in an amount less than that required for combustion is what is essentially involved in the pyrolysis process (Mohan, et al., 2006). Biomass can thereby be transformed into products of higher values which can be either used as intermediate energy carriers or actually fuels after improvement. The process would hence recover namely: *liquid fuel (bio-oil), solid fuel (biochar),* and *gaseous fuel (non-condensable gas)* (Danje, 2011). The spectra of products from different pyrolysis process, nevertheless, will depend on process conditions. The major parameters that would have this influence include the process *temperature, pressure, heating rate,* and *pyrolysis vapors' residence time* (Demirbas, 2004) (Bridgwater, et al., 1999). The figure below depicts simple representation of the process of biomass pyrolysis.

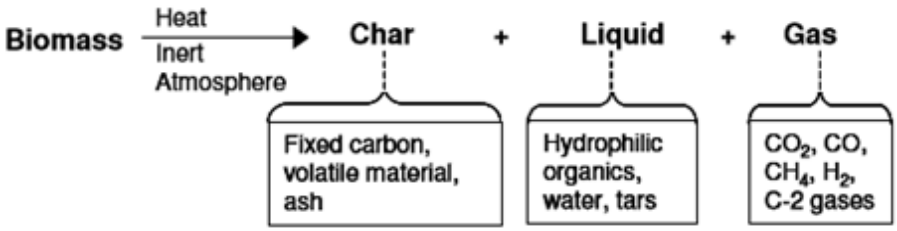


Figure 2-10 – Simple Representation of Biomass Pyrolysis Process
Source: (Riediger & Gerlach, 2010)

Complex interaction of heat and mass transfers is involved in the decomposition of biomass. Chemical reactions resulting in the evaporation of water and vapors, and production of some non-condensable gases also take place (Gronli, 2000).

The biochar consequently produced includes most of the minerals present in the biomass even though carbon is what it mainly consists of. The produced vapors can have a good portion condensed to bio-oil (usually a brown liquid) whereas the gaseous products which are non-condensable are left as fuels that can be combusted for immediate use (Danje, 2011).

Pyrolysis of biomass can also be seen as the initiation for combustion and gasification processes. Succeeding sequences involved in overall process are found in (Jones, 2011). The first step is heat transfer inwards to the material being pyrolyzed followed by the next step where decomposition reactions take place. Outward mass transfer of reaction products will then take place after which component molecules will mix with O_2 in the air resulting in combustion. However, in the absence of air pyrolysis ends prior to mixing with O_2 producing charcoal, tar (bio-oil), condensable liquids, and non-condensable gases. Figure 2-11 is a representation of this process showing the individual steps just mentioned.

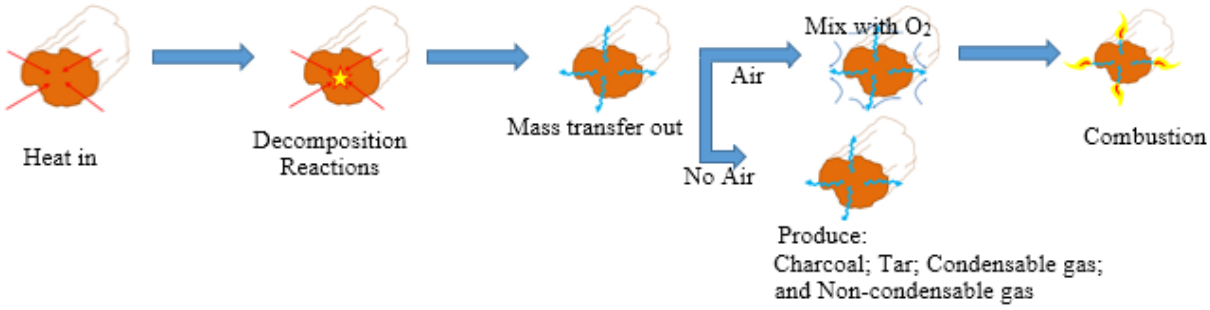


Figure 2-11 – Steps in Biomass Pyrolysis
Source: Compiled from (Jones, 2011)

Pyrolysis primarily includes consideration of input and process parameters, and observation of outputs/products (Figure 2-12). This is due to the varying effects of different process conditions and parameters. Influences from pyrolysis conditions are mainly reflected on the type and

amount of product as well as respective qualities. Temperature, heating rate, moisture content of feedstock, pressure, and time can be mentioned as the major variables to consider for significant influences on the pyrolysis process and its products.

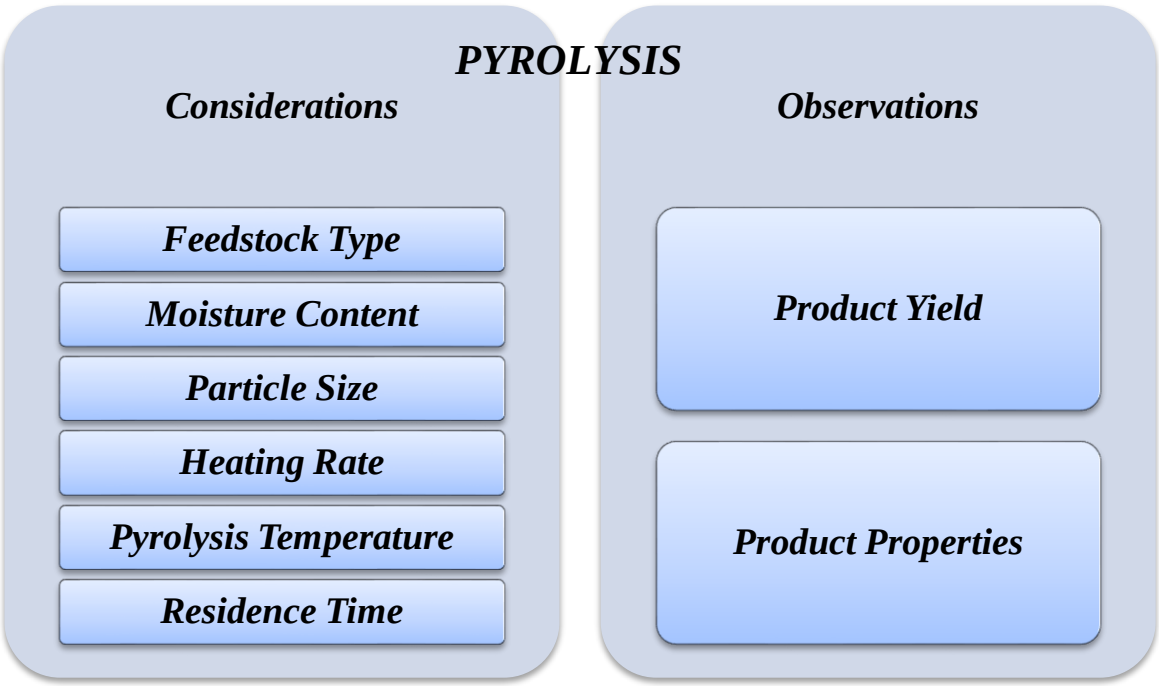


Figure 2-12 – Considerations and Observations in Biomass Pyrolysis
Source: (Jones, 2011)

Pyrolysis can have a variety of types such as *Torrefaction, Slow pyrolysis, Vacuum Pyrolysis,* and *Flash Pyrolysis*. Although all of these and other additional ones were thoroughly reviewed for the present study, *fast pyrolysis* of biomass – the method used in this study – is only included in this literature review. Elaborated discussions of the process and the effect of conditions are given below.

2.5.1 Fast Pyrolysis of Biomass

High heating rates and short vapor residence times prevail in "fast" pyrolysis. Small particle sizes of the prepared feedstock and design of the process that ensures quick removal of vapor from hot solids are generally required by this process. Fluidized beds, stirred or moving beds, and vacuum pyrolysis systems can be mentioned as only some of a number of reactor configurations that are available to achieve this. Stating in pyrolysis terms, a moderate temperature of around $500^{O}C$ is commonly reached (Begum et. al., 2012)

Development of fast pyrolysis methods progressed rapidly especially after the oil crisis in the 1970s when an indigenous renewable resource, mainly wood, was planned to be used as a way of producing liquid fuel from a process that is designed to give a high yield of bio-oil. According to Brownsort (2009, pp. 10-12), today several commercial processes such as Ensyn Corporation's Rapid Thermal Process (2009) or Dynamotive's Biotherm process are available and well-established as well.

Biomass raw materials are heated rapidly to a temperature between 450 and 500°C, in the absence of oxygen under which conditions they convert to organic compounds, vapors, non-condensable gases, and liquid tar. The organic vapors can be condensed thenceforth to produce a pyrolysis oil or bio-oil. In common practice, it has been possible to convert about 50–75% wt of the initial feed to bio-oil (Zafar, 2013).

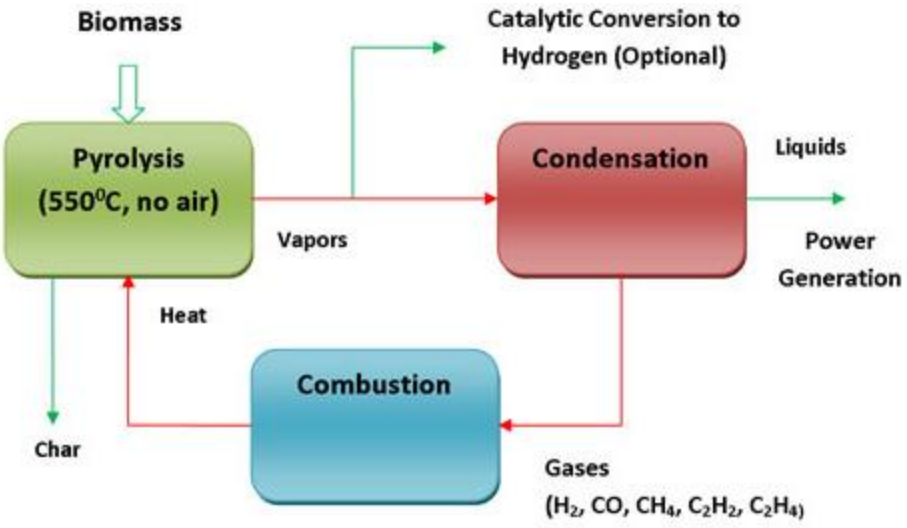


Figure 2-13 – Process Conditions for Pyrolysis of Biomass
Source: (Zafar, 2013)

As the entire process of fast pyrolysis goes on quickly it makes the role of not only chemical reaction kinetics but also mass and heat transfer processes and phase changes very significant. What is always important is to prepare the feedstock and put them through the process where an optimum temperature is maintained. At lower temperatures char production is favored which implies a need to reduce biomass' exposure to such intermediate temperatures – a goal that can be reached through the preparation of the feedstock into small particles (Vigouroux, 2001). Although different values are suggested in various literatures they can all be generalized to recommend a size of less than 1mm. Vapors and aerosols together with some (small) amounts of biochar are what fast pyrolysis of biomass principally generates. Quenching, cooling, and

condensation of the vapors and aerosols can also be done afterwards to obtain a bio-oil product – a dark brown liquid.

Production of bio-char and bio-oil are common in both conventional and fast pyrolysis. Fast pyrolysis, however, involves control and optimization of operating parameters to lead to high bio-oil yields – making it more advanced than conventional process.

Bridgwater and colleagues listed the following important features of liquid fuel production using fast pyrolysis (Bridgwater, et al., 1999).

- Since biomass generally has low thermal conductivity, finely ground feed (typically d_p < 3mm) is usually required for very high heating and heat transfer rates at the biomass particles' reaction interface.
- Pyrolysis and vapor phase temperatures of around 500^OC and 400^OC to 450^OC, respectively, need very careful and strict control.
- The residence time for vapor is short – typically < 2 sec.
- Acquiring the bio-oil product requires rapid cooling of pyrolysis vapors.

2.5.1.1 Effects of Process Conditions

The reactor and maintained conditions inside significantly affect yields and properties (hence qualities) of products. The major ones – heating rate, pyrolysis temperature, particle size, and vapor residence time – are briefly discussed below.

A. Pyrolysis Temperature

Different liquid yields from fast pyrolysis of most types of biomass are optimized within the temperature range of 450 – 500^OC (Yan et.al., 2011). Figure 2-14 below shows yield data from fast pyrolysis processes of wood carried out at different temperatures within the range of 400 – 600^OC. Temperature's influence on the spectra of products can be interpreted as favoring production of biochar and gas at lower and higher (> 500^OC), respectively.

Lower heating rates resulting from lower pyrolysis temperatures lead to the simulation of slow pyrolysis which is why solid fuel production is encouraged. Bio-oil products prevailed up until the pyrolysis temperature exceeds 500^OC. This is due to the phenomenon where production of non-condensable gases was favored in the process whose conditions inclined more towards those of gasification. Similar findings were also reported in several literatures

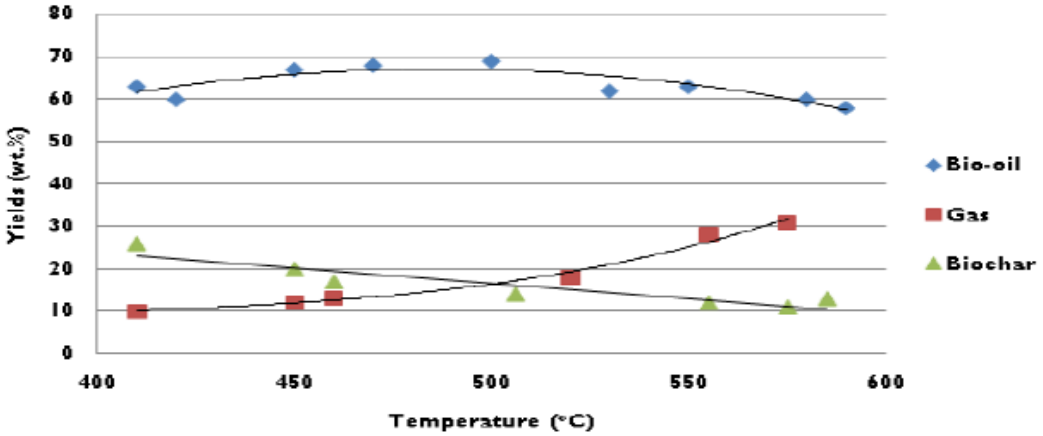


Figure 2-14 – Product Yields from Pyrolysis of Wood at Various Temperatures
Source: (Danje, 2011, p. 21)

Cellulose undergoes the following three principal reactions during pyrolysis (Van de Velden, et al., 2010):

1. *(T < 300°C) Dehydration (dominates) at low temperatures where the preferred products are bio-char, water, and gas.*

2. *(300< T < 450°C) Depolymerisation (dominates) where anhydrous sugar-like levoglucosan and oligosaccharides in tarry phase are produced, and;*

3. *(T ≅ 500^{O}C) Fragmentation to hydroxyacetaldehyde, acids and alcohols;*

Also occurring at lower temperatures of around < 400^{O}C is the formation of liquids of lower molecular weight as subsequent of condensation reactions. However, these reactions are subjected to major impacts from inorganic species including K, Na, Fe, and Al that may change cellulose's chemical and/or physical structure (Yan et.al., 2011)

A similar process is also followed in decomposition of hemicelluloses. Dehydration and depolymerisation take place at low (<180^{O}C) and higher (> 500^{O}C) temperatures, respectively. Products from hemicelluloses going through decomposition are reported to be anhydride fragments, biochar, gas, and water from dehydration; and furans, volatile organics, and levoglucosenone emerge from depolymerization (Danje, 2011) (Mayhead, 2010).

Lignin, on the other hand, undergoes a process in which dehydration dominates at temperatures of less than 500^{O}C whereas decomposition at higher temperatures forms lignin monomers. Nevertheless, it is noteworthy that lignin is the most thermally stable among the lignocellulosic components (Brownsort, 2009).

It is likely for pyrolysis reactions of larger particles for longer residence time to be exothermic while pyrolysis of small particles where immediate removal of vapor is involved is said to be endothermic (Ahuja, Humar, & Singh, 1999). However, the numerous types of reactions that are observed during pyrolysis can make the process either endo- or exothermic (Danje, 2011).

Yields and composition of gas products from fast pyrolysis are also affected strongly by temperature. It has been reported that high temperatures (> $500^{O}C$) not only yielded more gas product but also one rich in hydrogen whereas at temperatures lower that $500^{O}C$ biochar yields at higher percentages than gas. Furthermore, one of the main gas products from biomass degradation is reported to be CO_2 with very high concentrations at early stages of fast pyrolysis which primarily resulted from hemiellulose's relatively low conversion temperature (Vigouroux, 2001).

Summary of major reactions and products from fast pyrolysis of biomass at different temperatures is given in Table 2-5 below.

Table 2-5 – Reactions and Products' Spectra of Pyrolysis at Different Temperatures
Source: (Compiled from (Atadana, 2010), (Danje, 2011), and (Jones, 2011))

TEMPERATURE (^{O}C)	**REACTION**	**PRODUCTS**		
		Liquids	***Solids***	***Gas***
< 300	• Free radical initiation • Elimination of water • Depolymerization	Carbonyl compounds	Biochar	H_2O CO CO_2
300 – 450	• Breaking of glycosydic linkages of polysaccharides • Depolymerization	Mixture of levoglucosan, furans, aromatics, anhydrides and oligosaccharides in tarry phase	Biochar	CO_2, CO, CH_4, H_2, C_2H_4, C_2H_6, H_2O
450 – 500	• Dehydration, rearrangement and fission of sugar units	Carbonyl compounds such as acetaldehyde, vanillins, acids, alcohols, glyoxal and acrolein	Biochar	C_2H_4, C_2H_6, CO_2, H_2

TEMPERATURE (^{O}C)	REACTION	PRODUCTS		
		Liquids	***Solids***	***Gas***
> 500	• A mixture of all the above reactions	A mixture of all the above products		H_2

B. Heating Rate

Bio-oil yield increased with heating rate (Riediger & Gerlach, 2010). This same relationship between heating rate and yield of bio oil was reported by (Pinthong, 2009), (Paradela, et al., 2009), (Danje, 2011), and (Yan et.al., 2011) whose works involved fast pyrolysis of rice husk, forest biomass, corn residues and pine chips, respectively**.** Biochar production promptly decreased with fast rates of heating because solid particles pass the charring zone at lower temperatures more quickly which also led to improved production of bio-oil. At low heating rates, however, the process of slow pyrolysis is simulated resulting in the production of biochar as the primary (Brownsort, 2009).

C. Vapor Residence Time

Vapor residence time is the average time spent inside the reactor by a gas molecule. It is a function of volume of the reactor and flow rate of flashing gas (mostly N_2). Mathematically, it can be expressed as:

$$\tau = \frac{V}{Q} \qquad \textbf{(2.1)}$$

where:

τ = vapor residence time (s);

V = reactor volume (m^3); and

Q = flashing gas flow rate ($m^3.s^{-1}$)

The effect of residence time on liquid yield was studied where a rapid decrease in yield of bio-oil with more production of tars were reported to be caused by increased residence time (Scott, 1999) (Linden et al., 2005). The conclusion was that secondary reactions, cracking, and polymerisation resulted in the decrease.

On the other hand, Antal and colleagues studied the effect on composition of bio-oil. Polymerization was promoted as secondary reactions went on to ultimately increase the viscosity of the liquid product (Antal & Varhegyi, 1995).

Essentially, short residence time (< 2s) is recommended (Yaman, 2004) since secondary reactions of primary products resulted from longer residence time of vapors and elevated temperatures (> 500^{O}C).

D. Particle Size

Evolvement of all volatiles coupled with complete decomposition of feedstock particles can be said vital features of fast pyrolysis of biomass. Different literatures suggested that having smaller particle size (<2mm) will improve the efficiency of bio-oil production. It was also reported about increased biochar yield with a decrease in that of bio-oil resulted from increased particle sizes which also ended up in higher yields of non-condensable gases. The main reason for this was better heat transfer in the inner core of smaller biomass particles favored the production of bio- oil (Jones, 2011).

It could also be seen that particle size influenced the quality of bio-oil produced (Vigouroux, 2001). Smaller particles gave lower and higher yields of light and heavy bio-oil components, respectively. They also suggested that only particles of the same biomass and that are prepared using similar milling methods can be compared for the effect of their respective sizes on the behavior of fast pyrolysis process. Consequently, a need to categorize the different biomass types and find an optimum size for their prepared feedstock particles so as to maximize liquid yield and quality was also noted.

2.5.1.2 Feedstock Options for Biomass Fast Pyrolysis

Pyrolysis' notable advantage is the possibility of producing homogenous, clean and renewable biofuels from almost any kind of biomass. (Brownsort, 2009). A wide range of biomass feedstock can be used in pyrolysis processes including forest products wastes, agricultural residues, organic fractions of municipal solid wastes, paper, cardboard, plastic, food waste, green waste, and other waste. Biomass such as wood leaf, wood industry residues, rice husks and sawdust, and corn stalks were used as raw materials in scientific researches by (Zabaniotou & Karabelas, 1999), (Garcia-Perez, et. al., 2007), (Zheng, et. al., 2006), and (Yi, et al., 2000), respectively.

Drying is usually essential in the preparation of raw materials because high moisture content will reduce the heating value of bio-oil and affect its storage stability (Xu, et al., 2011). Less than 10% is thus suggested since at higher moisture contents, high volumes of water are produced and at lower levels there is a risk of the process producing only dust instead of oil.

That is why high-moisture waste streams, such as sludge and meat processing wastes, require drying before subjecting to pyrolysis (Vigouroux, 2001).

2.6 Pyrolysis of Biomass and Plastic Waste Mixture

Addition of plastics to the pyrolysis mix of biomass will enhance the production of liquid fraction. This improvement may be attributed to the betterment/amelioration in heat and mass transfer rates, due to the liquid phase that is more readily formed in the thermal cracking of plastics (Bajus, 2011).

Co-pyrolysis behavior of rice husk, waste plastics and their "blends" was researched with particular and in-depth study of the kinetics (Pinthong, 2009). The data obtained from a thermogravimetric analyzer (TGA) described the decomposition behavior of the materials and synergistic effect the mixture components exhibited to influence decomposition behavior of one another. They were used to determine the kinetic parameters (activation energy and pre-exponential factor). In the experiments waste plastics (WPL) and their "blends" with rice husk (RH) at WPL/RH ratios of 30/70, 50/50 and 70/30 were used. It was reported that these mixtures had synergy for conversion at around 485^{O}C. The main product from pyrolysis of all mixtures at 485^{O}C was wax. The WPL/RH ratio of 30/70 showed the highest synergy and was chosen to be further pyrolyzed with zeolite (H-ZSM-5) catalyst. Liquid product from the catalytic pyrolysis contained almost no wax had higher heating value than the wax product. The liquid product was distilled and yielded these percentage volumes of the following products gasoline 54.54%, kerosene 24.24%, diesel 15.15%, and residue 16.06%.

A mixture of wood and synthetic polymers was also used to study their co-pyrolysis (Sharypov, et al., 2002). The biomass component of the feedstock in their study contained beech wood, pine wood, cellulose, and hydrolytic lignin while medium density PE, and isotactic and atactic PP were the polymers selected as raw materials. It was reported that high yield of light distillate fraction and benzene soluble products was obtained from co-pyrolysis of the different type of natural and synthetic mixtures in an inert atmosphere. A temperature of 400^{O}C was found to be the optimum at which the feed mixture yielded the maximum light liquid.

Furthermore, biomass, plastics, and used tyres were put to the test to study their pyrolysis (Paradela, et al., 2009) . Specifically, the effects of process conditions on yield and composition of products were investigated. The influence of pyrolysis temperature thus reported led to an increase in the alkane content of gas products (from 39 to 70% vol.), but reduced the liquid

yield (from 82 to 73% wt.) while gas and solid yields increased with it. Alkane content both in gas and liquid products increased with increased pyrolysis time – from 53 to 70% vol., and from 48 to 60% wt., respectively. Nevertheless, amount of plastics in the feed mixture had the most influence on products' yield and composition. Liquid yield increased with this parameter (from 33 to 92% wt.) at the cost of reduced solid and gas products, and decreased aromatics (from 52 to 28% wt.)

Fast pyrolysis of biomass has been widely studied to produce a liquid product from woody materials, with adequate fuel properties, in contrast to the typical slow pyrolysis method of carbonization to produce char. However, some properties of this bio-oil restrict its direct use in a diesel engine, so research is still going on to improve the properties (bio-oil upgrading). In addition, there has been some investigation on the formation of liquid products with commercial interest. (Paradela, Pinto, Gulyurtlu, Cabrita, & Lapa, 2008).

3. MATERIALS AND METHODS

This chapter deals with the materials and methods used for the study. Details of the approaches employed in different parts of the research where data were generated and analyzed are also included in this chapter.

3.1 Materials

Materials used for feedstock in the pyrolysis experiments of this study were *khat* waste (garaba), and waste HDPE. The *khat* waste was acquired from a small-scale outlet located in Yeka Sub-City opposite St. Michael Church on the road to CMC where *khat* was sold, and several customers regularly came to chew there.

HDPE wastes, on the other hand, were obtained from a small retail shop also found in Yeka Sub-City on the road to Megenagna from Adwa Bridge. Plastic bags made from HDPE were used in large quantities to package some spices and raw food stuff that were sold there. A good amount of scrapped and damaged HDPE was collected to be used in this study.

Nitrogen gas (> 99.6%) was purchased from Chora Gas and Chemicals PLC. A removable cap fitted with a rubber hose which connected it to the N_2 cylinder was placed at the reactor inlet to flash the prepared batch for pyrolysis for 2 minutes. This method was used before each run so as to attain an inert atmosphere in the reactor prior to its sealing and insertion in the furnace for heating.

List of equipment, and instruments employed for all laboratory applications that were involved is given in Table 3-1 below while Table 3-2 that follows shows chemicals that were used.

Table 3-1 – List of Equipment and Instruments Used

APPLICATION	EQUIPMENT	MANUFACTURER (MODEL)
Preparation of Raw Material		
Size reduction of dried khat waste	Mill	Metalurgica Trappa Ltd., Brazil (TRF300C)
Preparation of fine khat ($d_p \leq$ 1mm)	Sieve	Retsch, Germany (AS200)
Drying khat samples for pyrolysis	Oven	Memmert, Germany (100-800)
Determination of moisture content of khat for pyrolysis feed	Digital Moisture Content Measurement Device	Ohaus, Switzerland (MB45)
Characterization of Khat Waste		
Boiling acid mixture in lignocellulosic analysis	Water Bath	China, (HWS26)
Measurement of ash content	Furnace	N/A
Measurement of apparent density	Pycnometer	N/A
Determination of energy content of dried khat waste	Bomb Calorimeter	Cussons technology, England.
Pyrolysis Process		
Reactor for pyrolysis	Stainless steel tube	N/A
Heating pyrolysis mixture	Furnace	Carbolite, England (MF03-V3.11)
Condensation of pyrolysis vapor	Condenser	N/A
Cooling and circulation of water for condensation	Chiller	N/A
Characterization of Liquid Product		
Measurement of viscosity for liquid product samples	Falling (Glass) Ball Viscometer	Gilmont Instruments, USA (GB-104234)
Separation of liquid product fraction during solvent extraction	Separating Funnel	N/A
Miscellaneous		
Measurement of mass	Digital balance	Ohaus, Switzerland (EP 214C)
Filtration of acid solution for determination of lignocellulosic content;	Vacuum pump	KNF Laboport
Determination of lignocellulosic composition	Glass Crucibles and vacuum filtration setup	N/A

Table 3-2 – List of Chemicals Used

APPLICATION	CHEMICAL
Characterization of Khat Waste	
Solvent in lignocellulosic analysis	HNO_3
Solvent in lignocellulosic analysis	H_2SO_4
Solvent in lignocellulosic analysis	CH_3COOH
Solvent and stripper in lignocellulosic analysis	CH_3OH
Solvent and stripper in lignocellulosic analysis	Distilled Water
Application of bomb calorimeter	Oxygen
Pyrolysis Process	
Flash pyrolysis	N_2
Pyrolysis feed	Khat Waste
Pyrolysis feed	HDPE
Cooling fluid for condensation	Water
Insulation of reactor's parts and elbow fitting to minimize heat loss	Fiber Glass
Miscellaneous	
Cleaning of used experimental appliances	Chrome Solution

3.2 Methods

3.2.1 Preparation of Feedstock

Khat and HDPE wastes were first washed to remove dust and/or other sediments that otherwise could contaminate the materials. They were then placed on open trays and kept in the sun for few hours until they dried enough to undergo size reduction in a mill. After milling *khat* waste particles that passed through the 1 mm tray during sieving were collected. For HDPE, however, particles were manually prepared using mechanical paper presser that cut the plastic into small circles of around 2mm in diameter.

The waste materials were then dried. For HDPE, because the need was only to remove moisture added after washing, simple solar drying was used. Whereas fine particles of *khat* waste were dried using a ventilated oven. *Khat* particles used in all experiments were also stored in the oven at $105^{O}C$ so that a moisture content $\leq 10\%$ was achieved. By so doing it was possible to maintain a-less-than 5% moisture for all runs (typically between 2.96 and 4%). The moisture content of samples of *khat* used in pyrolysis was determined by using a measuring instrument.

Components of feeds for pyrolysis experiment – *khat* and HDPE wastes – were finally mixed manually at the beginning of each run. Feeds for respective runs of the experiment were prepared in such a way where respective percentage compositions of *khat* were 30, 70, or 100% depending on the specific level of this factor for a run.

3.2.2 Characterization of Khat

Khat was characterized using different properties which were determined at respectively convenient incidents – prior to, alongside, or after runs. The methods used to determine parameters that were used to characterize *khat* waste are briefly discussed below.

3.2.2.1 Density

Oven dried *khat* samples were measured for bulk and apparent densities using procedures as per respective ASTM standards.

A. Bulk Density

Bulk density was determined by packing oven-dried *khat* sample of known mass into a graduated cylinder according to ASTM procedure (D 6683)**.** The cylinder was then tapped until compaction was observed visually. The bulk density was then calculated by using the volume of the cylinder filled up by the sample in the following equation:

$$Bulk\ Density\ of\ khat\ \left(\frac{kg}{m^3}\right) = \frac{mass\ of\ khat\ sample\ (kg)}{volume\ of\ khat\ sample\ (m^3)} \quad \textbf{(3.1)}$$

B. Apparent Density

Standard procedure (ASTM D 854) was followed in the determination of apparent density for which a 25-ml pycnometer was used. In the procedure, oven-dried *khat* sample was put into the container up to the level of approximately a third of the total height. Next, distilled water was poured until it filled the remaining volume of the vessel. The rationale behind addition of water was that it would fill up all voids so that calculating volume of *khat* sample could be done with the best possible precision. Weighing the mixture hence gave the combined mass of the pycnometer, *khat* sample, and water. The volume of *khat* was found by subtracting the volume of distilled water used from the total volume of the pycnometer.

$$\rho_{apparent} = \frac{m_{khat}}{V_{khat}} \quad \textbf{(3.2)}$$

$$V_{khat} = V_{pycnometer} - V_{water} \quad \textbf{(3.3)}$$

$$V_{water} = \frac{m_{water}}{\rho_{water}} \quad \textbf{(3.4)}$$

$$m_{water} = m_{total} - (m_{vessel} + m_{khat}) \quad \textbf{(3.5)}$$

Therefore, from these equations the apparent density of *khat* was calculated as follows.

$$\rho_{apparent} = \frac{m_{khat}}{25ml\ - V_{water}}. \quad \textbf{(3.6)}$$

3.2.2.2 Moisture Content

A weighed sample of *khat* was placed in a ventilated oven where a temperature of 105.3^{O}C was maintained in accordance with ASTM standard D 2395–02. Dried sample from the oven was withdrawn and weighed every 3 hours until readings confirmed no significant loss of mass. The moisture content (in percent) was calculated according to equation (3.7).

$$\%Moisture = \left[\frac{(m_{initial} - m_{oven\ dried})}{m_{initial}}\right] \times 100\% \quad \textbf{(3.7)}$$

3.2.2.3 Ash Content

Similarly, ASTM standard D 1102 – 84 was referred to determine ash content. Oven-dried *khat* sample was weighed, placed in a ceramic crucible to be put in a furnace. It was kept for 4 hours in the furnace at 600^{O}C. Mass of the remaining ash was measured and the initial mass of *khat* sample was divided by the result to calculate percentage content of ash as follows:

$$\%\ \text{Ash} = \left[\frac{m_{ash}}{m_{initial}}\right] \times 100\% \quad \textbf{(3.8)}$$

3.2.2.4 Elemental Analysis

Dried *khat* sample was analyzed for its CHNS composition. The measurement of respective percentage amounts was done on an automatic elemental analyzer *(MODEL: Thermo Scientific – FlashEA1112)* at the Chemistry Department of College of Natural Sciences.

3.2.2.5 Lignocellulosic Composition

Amounts of cellulose and lignin were determined following standard procedures given in (Pereira, 1988), and ASTM D 1106 – 96, respectively.

A. Cellulose

An acid solution was prepared by mixing H_2SO_4 and CH_3COOH. A weighed sample of oven dried *khat* was then put in the vessel containing this solution. The mixture was kept in a water bath that was maintained at 40^OC for 35 minutes. After allowing it to settle for few minutes, the heated mixture was transferred on to glass crucible where it was filtered and simultaneously washed by CH_3OH. The crucible was dried in an oven and percentage composition of cellulose was determined as seen below.

$$\%\ Cellulose = \left(\frac{m_{dried\ khat\ +\ cruicible} - m_{empty\ crucible}}{m_{initial\ khat\ sample}}\right) \times 100\% \quad \textbf{(3.9)}$$

B. Lignin

Percentage of lignin, on the other hand, followed a similar procedure. *Khat* sample was dissolved in 72% H_2SO_4 solution and left to stand for 2 hours after it was continuously stirred for about 1 min. The acid concentration was brought down to 3% by adding 560 ml of distilled water and the resulting solution was boiled in the water bath for 4 hours before being washed by distilled water during filtration. After oven drying the crucibles for 24 hours at 105^OC, the lignocellulosic contents were calculated as follows.

$$\%\ lignin = \left(\frac{m_{dried\ cruicible} - m_{empty\ crucible}}{m_{initial\ khat\ sample}}\right) \times 100\% \quad \textbf{(3.10)}$$

3.2.3 Pyrolysis Process

All experiments were conducted at the process engineering laboratory of AAiT's School of Chemical and Bio-Engineering in an assembled setup that used a tubular type of rector heated in a tubular furnace. A stainless tube ~ 1 m long with an internal diameter of ~ 0.05 m was utilized. The furnace employed could reach a maximum temperature of 1200^OC and it was possible to reach a maximum heating rate of $100^OC.\ min^{-1}$.

All runs in the experimentation of this research were conducted in a batch process of fast pyrolysis. The prepared raw materials for an experiment were fed into the tubular reactor which was inserted into a tubular furnace. The reactor was then flashed with N_2 gas so as to make the environment inside inert. This had a strong effect in minimizing partial combustion reactions and hence the emergence of their products.

A constant heating rate of $100^OC\ min^{-1}$ was used for all experiments mainly because the furnace used did not allow any further increment from this value. For fast pyrolysis, however, a much

greater rate was required – as high as 1000 K. min^{-1}. A single pyrolysis run was conducted at either one of the three levels of temperature – 550, 650, or 750^{O}C and carried on for long enough time to attain 30 or 60 minutes of vapor residence time. The value set for a run's temperature and time followed the randomized order as per the experimental design.

A shell and tube glass condenser 0.3 meters long was installed downstream the reactor. An elbow fitting made of glass was used for connection and it was insulated using fiber glass to avoid condensation of pyrolysis vapor on its walls prior to entering the condenser.

Water was used as the cooling medium which circulated through the condenser tube. A chiller was used to cool it down to 4^{O}C, and pump it to the condenser.

Finally, liquid condensate was collected as the fuel product using a small glass container that was held sealed to the end of the condenser. Figure 3-1 shows schematic representation of the experimental setup used for this research.

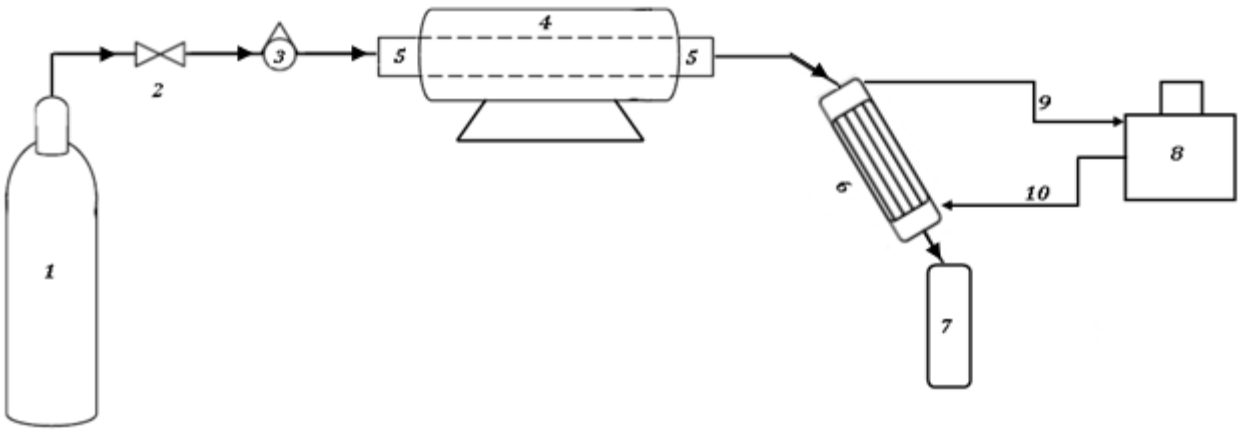


Figure 3-1 – Schematic of Lab Setup for Experiments

LEGEND

1. N_2 gas cylinder	6. Glass Condenser
2. Valve	7. Product (condensate) collector
3. Pressure gauge	8. Chiller
4. Tubular Furnace	9. Hot water to chiller
5. Stainless Steel Tube Reactor (inserted into the furnace)	10. Cooling Water (at 4^{O}C) to condenser

3.2.4 Analysis and Characterization of Product

Primarily liquid products and bio-chars, from each experiment were collected and measured for different parameters. Respective measurements and computations were used to generate

data of yield, and other properties. Succinct descriptions of these analysis and characterization methods are given below.

3.2.4.1 Yield

Percentage yield of liquid fuel products from each experiment run was calculated using the following formula:

$$\%Yield\ of\ liquid\ fuel = \left(\frac{m_{liquid\ (condensate)}}{m_{pyrolysis\ feedstock}}\right) \times 100\% \quad \textbf{(3.11)}$$

The reactor was emptied after every run to collect char product inside, and solidified oil (wax) that remained on its walls. Respective masses measured after weighing the samples were then used to estimate the amount of non-condensable (NC) gas product from the experiment.

$$m_{NC} = m_{pyrolysis\ feedstock} - \left(m_{liquid} + m_{char}\right); \quad \textbf{(3.12)}$$

3.2.4.2 Density

Products were put in graduated glass cylinders until it was filled to its known volume. Masses of liquid fuel samples from experiments were then used to determine the product's density using the relation below.

$$\rho_{liquid\ fuel}(kg/m^3) = \frac{m_{liquid\ sample}}{V_{liquid\ sample\ (cylinder)}} \quad \textbf{(3.13)}$$

3.2.4.3 Viscosity

Falling ball method was used to determine viscosities of samples. In this method, a sample was transferred to a graduated cylinder containing the ball. Time taken by the ball to fall the height through the medium was recorded. The following relation was used to calculate the viscosity using the time data.

$$\mu = K\left(\rho_f - \rho\right)t \quad \textbf{(3.14)}$$

where; μ=viscosity **(**cp**)**;
ρ_f=density of ball (2.53 g/ml);
ρ=density of liquid (1.1 g/ml);
t=time of descent (minutes);
K=viscometer constant (0.3);

3.2.4.4 Heating Value

The energy content of liquid samples could not be determined using the bomb calorimeter. High moisture content in the sample and improper functioning of the equipment were suspected as possible reasons. However, it was given in works like (Sadaka, 2008) and (Sadaka & Boateng, 2009) and others that the elemental composition of bio-oil from pyrolysis is similar to that of the parent biomass.

The relations shown in equations 3.15 and 3.16 below were hence used to calculate the HHV and LHV of the selected sample (which was from 100% *khat*) using the elemental composition of *khat* waste.

$$HHV\ (kJ/kg) = 338.2(\%C) + 1442.8\left(\%H - \frac{\%O}{8}\right) \quad \textbf{(3.15)}$$

$$LHV\ (kJ/kg) = HHV - 218.3(\%H) \quad \textbf{(3.16)}$$

where %C, %H, and %O were to be from elemental analysis of khat waste

3.3 Experimental Design

3.3.1 Studied Factors

Experimental factors used for the study were selected primarily on basis of the objective set to identify the influence(s) of major process conditions in pyrolysis. Due to the high essentiality of their influences on pyrolysis processes, temperature and time were automatically included in the factors list (Samolada et al., 1990). On the other hand, as this research was the first of its kind to study about *khat's* pyrolysis, its percentage composition in the feed was included as the third factor. Effects of the following experimental factors were thus studied:

A. *Composition of khat waste in the feed mixture – kh (%);*
B. *Pyrolysis temperature – T (^{O}C); and*
C. *Total pyrolysis time – t (min.).*

Each of the first two had three levels while pyrolysis time was varied between two levels as shown in the table below. A total of 18 runs were required to complete the experiment (numbers shown in the cells show randomized run order). The total mass of the feed mixture used in all conducted pyrolysis runs was maintained at 50 grams.

Table 3-3 – Experimental Factors and Corresponding Levels

		Factor C: Pyrolysis Time (t)					
		L1 = 30 min			***L2 = 60 min***		
		Factor A: Khat percentage in feed (%kh.)					
		L1 = 30%	***L2 = 70%***	***L3 = 100%***	***L1 = 30%***	***L2 = 70%***	***L3 = 100%***
Factor B: Pyrolysis Temperature (T)	***L1 = 550^{O}C***	(14)	(18)	(10)	(4)	(9)	(17)
	L2 = 650^{O}C	(2)	(15)	(7)	(6)	(16)	(11)
	L3 = 750^{O}C	(5)	(12)	(3)	(13)	(8)	(1)

Furthermore, there were other process conditions which had significant respective influences but not included in this study. Factors that were not studied and corresponding reasons for exclusion were:

1. *Pressure*: Lack of required facility that allowed setting, monitoring, and controlling.
2. *Heating Rate*: Absence of feature in the employed furnace that enabled application of heating rates greater than 100^{O}C per minute while fast pyrolysis process, however, required much higher values.
3. *Moisture content of the feed*: The effect of moisture content was widely reported in numerous literatures stating its inversely proportional relationship with liquid yield from pyrolysis of biomass.
4. *Particle Size:* It has been commonly reported that large feed particles (> 1 – 2mm) favored production of bio-char at the cost of reduced bio-oil production.

3.3.2 Selected Type of Experimental Design and Analysis

The desirability to identify the effect(s) of various operating parameters when studying a process is emphasized. Techniques that are commonly used to know such influences on the response involved varying one factor at a time while the others remain constant – the OFAT method; or using factorial designs approaches. While the former had the evident pitfall of overlooking effects due to multiple factors' interactions, factorial design offered the most effective and efficient technique for obtaining reliable results and valuable information, especially in engineering research including interaction effects. Therefore, a factorial design approach that enabled the inclusion and analysis of multiple factors at multiple levels was

preferred. Multifactor RSM design (D-Optimal RSM) was hence used to design the experiment and analyze generated response data.

RSM approach enabled the analyses of influences from factors' interaction in addition to main effects (Montgomery, 2009). Not only that but it also helped to further quantify the relationships between one or more measured responses and the vital input factors (Stat-Ease, Inc., 2007).

The experimental design and analysis of data, as well as the regression computations to statistically fit the response and factors' into a model made use of the software package Design-Expert® 7.1. Accordingly, 18 runs were sufficient to provide information about the effect of each factor on the yield of pyrolysis liquids which was considered as the response. The effects of *khat* composition in the feed, pyrolysis temperature, and pyrolysis time on the percentage yield from the experiment runs were thus studied. The output from the software showing a summary of the design is given below.

Design Summary

Study Type	Response Surface		**Runs**	18	
Initial Design	D-optimal	Point Exchange	**Blocks**	No Blocks	
Design Model	Quadratic				

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded	Mean	Std. Dev.
A	Khat Comp.	%	Numeric	30.00	100.00	-1.000	1.000	66.667	28.674
B	T	deg.C	Numeric	550.00	750.00	-1.000	1.000	650.000	81.650
C	time	min	Categoric	30	60			**Levels:**	2

Figure 3-2 – Summary of the Experimental Design
(Output from DesignExpert Software)

3.4 Limitations

The purchase and installment of a number of equipment was proposed to ensure comprehensiveness of the study's experiment. However, the budget allocated by the institute for the research was significantly inadequate that inclusion of even basic parts of the entire planned work was considerably constrained.

4. RESULTS AND DISCUSSION

4.1 Characterization of Khat Waste

A number of physical and chemical characteristics of *khat* waste were identified. Results from respective analyses that were used to characterize *khat* waste are given in Table 4-1 below.

Table 4-1 – Characteristics of Khat

Proximate Analysis (% wt.)	
Moisture (as discarded)	76.3
Ash	5.31
Chemical Components (% dry basis)	
Cellulose	59.0
Lignin	31.7
Physical Properties	
Bulk Density	0.42 g/cm^3
Apparent Density	0.52 g/cm^3
Ultimate Analysis	
% C	47.12
% H	6.0
% N	1.23
% O (determined by difference)	45.65
HHV	17.46 MJ/kg
LHV	12.57 MJ/kg

These results were compared with corresponding values given in literatures for other biomass particularly with those reported for food and fiber processing wastes. It was thus shown that *khat* waste had very high moisture while its percentage ash content was found to be around the average. Lower amount of organic liquid product could thus be expected from pyrolysis of as discarded *khat* waste due to the very high moisture contained. The lower ash content whereas indicated more positive suitability of *khat* waste in thermochemical conversion due to the prevalent organic nature it affirmed.

The lignocellulosic composition values inferred that *khat* waste had relatively higher amount of cellulose and lignin. Comparing values reported in several consulted literatures, 38–46%

cellulose, and 16–28% lignin were found to be the average composition ranges for woody materials in general (Sadaka, 2008) (Sinha, et al., 2004) (Atadana, 2010) (Vigouroux, 2001). These components are further responsible for the variety and complexity of products formed during the pyrolysis of biomass. Above $300^{O}C$, cellulose breaks down to give tarry products containing low sugar derivatives and little char while lignin is condensed to carbonaceous char and gives smaller amounts of pyrolyzate containing phenolic compounds (Sadaka, 2008, p. 10). These phenomena implied that less amount of liquid product may be expected from pyrolysis of *khat* at temperatures > $300^{O}C$. Gas and char products, correspondingly, become higher due to higher amounts of cellulose and lignin.

The elemental analysis results showed that respective compositions of C, H, O, and N were fairly similar to most biomass wastes (Jenkins & Ebeling, 1995). The absence of S along with the very small amount of N, moreover, indicated that using *khat* waste in a thermochemical conversion process have insignificant production of NO_x and SO_x to pose any pollution threat.

4.2 Pyrolysis Results

The amounts of solid (bio-char), liquid, and gas products obtained from each run are given in the following table.

Table 4-2 – Products from Pyrolysis Experiments

RUN	***EXPERIMENTAL FACTORS***			***MASS OF PRODUCTS (G)***		
	% kh	***T (^{O}C)***	***t (min)***	***Solid***	***Liquid***	***Gas[1]***
1	100.00	750	60	23.6	13.00	13.40
2	30.00	650	30	11.9	2.20	35.90
3	100.00	750	30	35.1	11.50	3.40
4	30.00	550	60	15.9	12.50	21.60
5	30.00	750	30	10.6	1.50	37.90
6	30.00	650	60	4.5	2.80	42.70
7	100.00	650	30	26.4	11.10	12.50
8	70.00	750	60	13.1	9.10	27.80
9	70.00	550	60	12.5	6.70	30.80
10	100.00	550	30	17.1	9.70	23.20
11	100.00	650	60	25.6	12.00	12.40
12	70.00	750	30	11.79	9.00	29.21
13	30.00	750	60	10.6	1.50	37.90

RUN	EXPERIMENTAL FACTORS			MASS OF PRODUCTS (G)		
	% kh	T (^{O}C)	t (min)	Solid	Liquid	Gas[1]
14	30.00	550	30	16.8	10.90	22.30
15	70.00	650	30	12.5	5.00	32.50
16	70.00	650	60	12.5	5.00	32.50
17	100.00	550	60	16.61	10.40	22.99
18	70.00	550	30	13.3	6.20	30.50

[1]*Estimated by difference*

The maximum liquid fuel produced (13.0g) was when 100% of *khat* waste was pyrolyzed at 750^{O}C for 60 minutes *(Run #1)*. Solid product was also maximum for the same temperature and *khat* percentage but when pyrolysis went on for 30 minutes *(Run #3)*. The highest amount of gas, on the other hand, was produced when 30% *khat* was pyrolyzed at 650^{O}C, for 60 minutes *(Run #6)*.

4.3 Effect of Processing Conditions on Product Distribution

Amount of *khat* in the feed composition and pyrolysis temperature significantly influenced the distribution of products both separately (main effects) and interacting (interaction effects). Pyrolysis time, however, had the minimal influence on the product spectra obtained. Very small variations were observed between the amounts of products obtained from respective pyrolysis experiments that ran only for different times while the amount of *khat* and temperature remained the same.

Effects on product distribution from variations in feed composition and pyrolysis temperature are discussed under 4.3.1 and 4.3.2 below. Moreover, Figure 4-1 that follows gives a set of graphs showing plots of temperature versus amount of products obtained at various percentage compositions of *khat* in feed for the same 60 minute of pyrolysis time.

4.3.1 Effect of Feed Composition

Solid product (bio-char) increased mostly when more *khat* and less HDPE were pyrolyzed while inclusion of more HDPE in the feed gave relatively higher amount only at 550^{O}C. In general, amount of char produced seemed to increase with an increase in percentage composition of *khat* in the feed mixture.

The amount of lignin obviously increased as more *khat* was included in the feed mixture. Furthermore, the decomposition of this biomass constituent takes place when heated beyond 280^{O}C producing greater char than liquid and gaseous products at elevated temperatures (typically > 500^{O}C) (Sinha, et al., 2004) (Prakash & Karunanithi, 2008). The increase in production of char at higher temperatures and greater amount of *khat* in this study was, thus, explained using this thermochemical conversion property of lignin.

4.3.2 Effect of Pyrolysis Temperature

Liquid production increased considerably with increasing temperature during the pyrolysis of 70% and 100% of *khat*. When less *khat* was pyrolyzed, however, higher amount of liquid was produced at 550^{O}C while its production at the rest of the temperatures were very low. Production of gas, on the other hand, decreased as the amount of *khat* in the feed increased. Nevertheless, gas product dominated the entire product spectra at all temperatures and *khat* percentage except when the feed did not contain any HDPE.

The production of higher amount of liquid at 550^{O}C and 30% *khat* was because of the greater plastic present in the feed which normally degrades starting from temperatures as low as 400^{O}C. In addition, increased liquid at higher temperatures and more *khat* was attributed to the pyrolysis behavior of cellulose. It was investigated by (Mayhead, 2010) that char, tar, and gaseous products form when cellulose is pyrolyzed at temperatures > 300^{O}C. Laevoglucosan made up most of the tar produced.

The abundance of gas product observed in this study, on the other hand, was attributed mainly to further vaporization and decomposition of leavoglucosan as pyrolysis temperature increased according to what is reported by (Shafizadeh, 1992) who studied the pyrolysis of cellulose as temperature increased. However, inadequate condensation was also considered as the possible reason for this. Unsuitability of condenser size and hence insufficient condensation may also have led to the escape of volatiles to be taken as non-condensable portions of the gas product as suggested by (Agblevor & Besler-Guran, 2002).

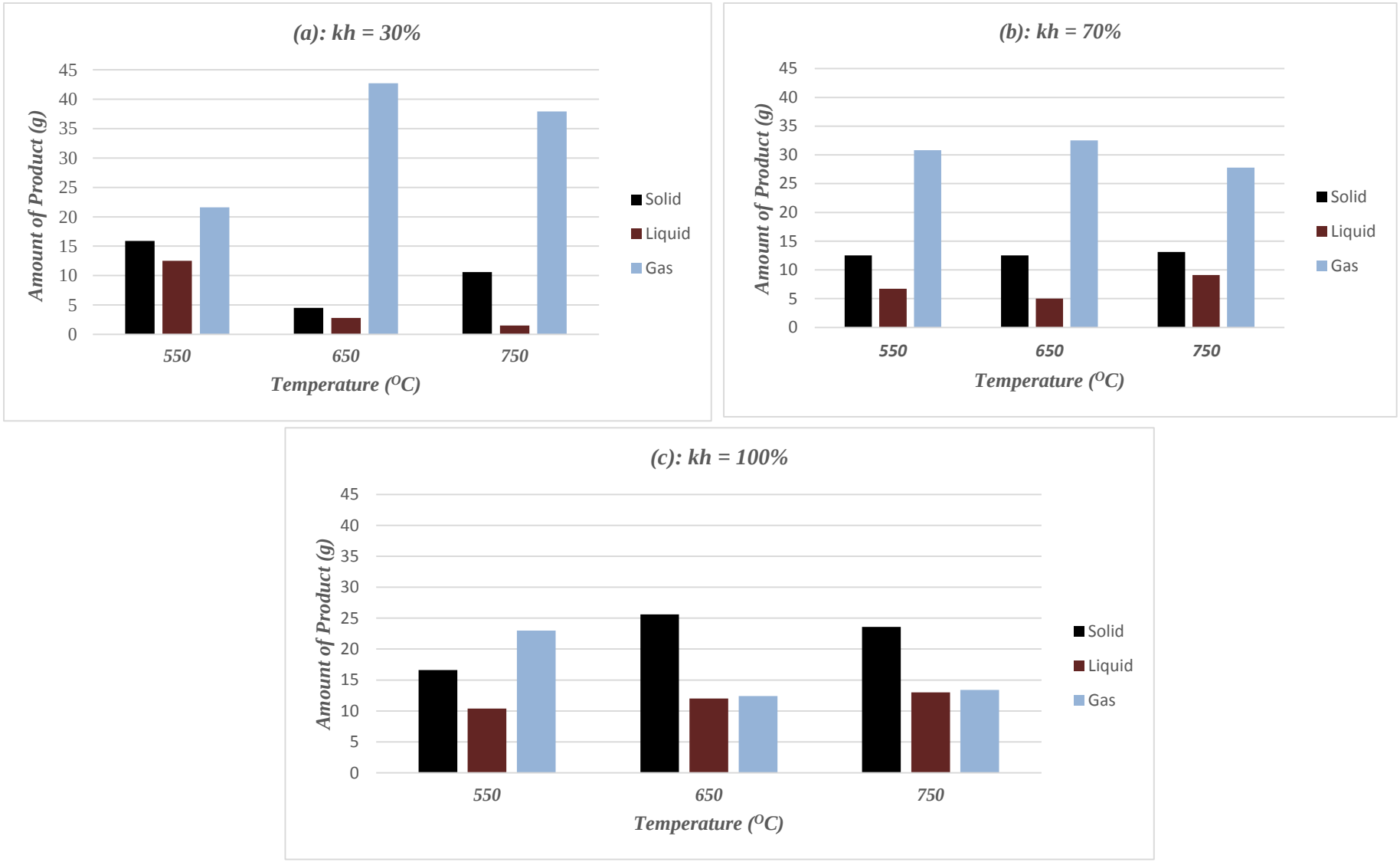


Figure 4-1: Amount of Products from Pyrolysis at Different Temperatures for 60 minutes (separate plots for different amount of khat percentage used in feed)

4.4 Liquid Fuel Yield

Data for percentage yield were generated as per equation (3.11) given in section 3.2.4.1. Percentage yield varied within the range of 3% to 26% with an average of 15.57%. The minimum and maximum percentage yields were from pyrolysis at 750^{O}C when the feed was composed of 30% and 100% *khat*, respectively (See Table 4-3 below).

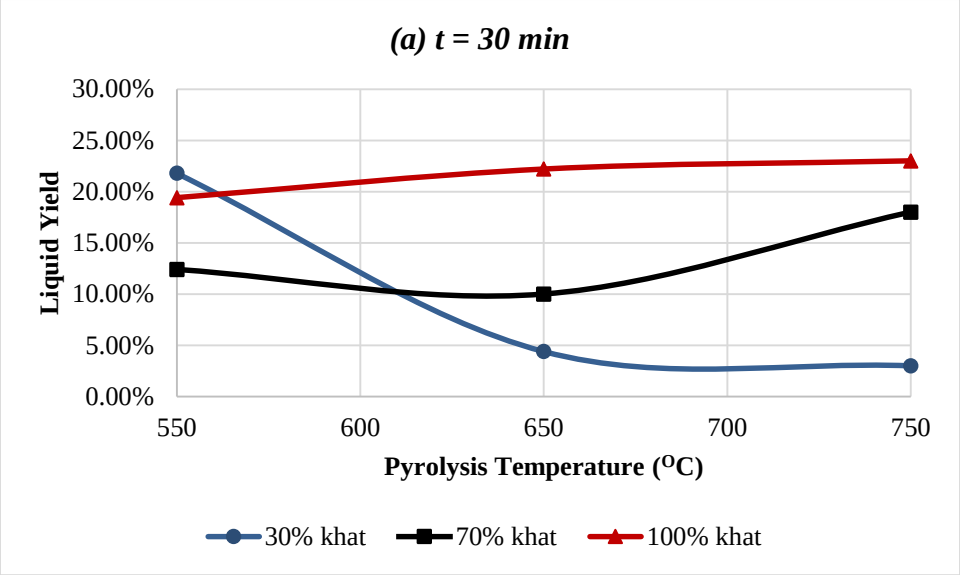
Table 4-3 – Liquid Fuel Yield at Different Processing Conditions

RUN	FACTORS			LIQUID YIELD (%)
	kh (%)	*T (^{O}C)*	*t (min)*	
1	100.00	750	60	26.00
2	30.00	650	30	4.40
3	100.00	750	30	23.00
4	30.00	550	60	25.00
5	30.00	750	30	3.00
6	30.00	650	60	5.60
7	100.00	650	30	22.20
8	70.00	750	60	18.20
9	70.00	550	60	13.40
10	100.00	550	30	19.40
11	100.00	650	60	24.00
12	70.00	750	30	18.00
13	30.00	750	60	3.00
14	30.00	550	30	21.80
15	70.00	650	30	10.00
16	70.00	650	60	10.00
17	100.00	550	60	20.80
18	70.00	550	30	12.40

4.5 Effect of Processing Conditions on Liquid Fuel Yield

Percentage yield data obtained was plotted against pyrolysis temperature for the various percentage compositions of *khat* used. Corresponding figures for the different pyrolysis times used are shown in

Figure **4-2** below.



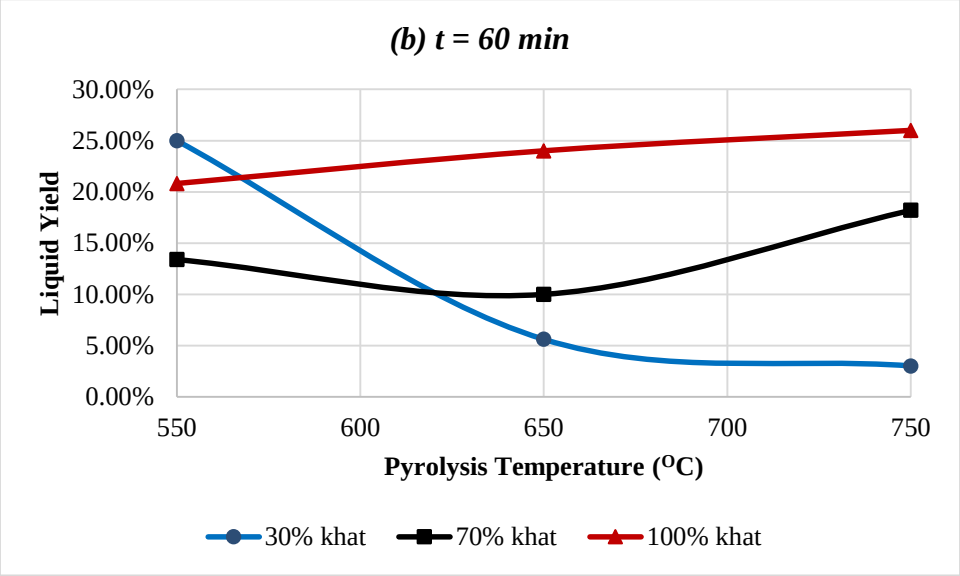


Figure 4-2 – Plots of Liquid Yield vs. Pyrolysis Temperature

4.5.1 Effect of Pyrolysis Time

The insignificant effect of pyrolysis time can be seen from the above set of graphs which showed very close similarity. It indicated that decomposition of both components of the waste mixture took shorter than 30 minutes. This phenomenon was also observed during conduction of runs through the initiation of gas and liquid products which started within an average time of 16 minutes after the start of pyrolysis process. The maximum time taken until no more condensation took place was around 20 minutes. The same minimal influence from pyrolysis time was reported by Paradela and coworkers who studied the pyrolysis of pine and plastic waste mixture (Paradela et al., 2008).

4.5.2 Effect of Waste Composition and Pyrolysis Temperature

The change in percentage yield due to varying temperature and waste composition was studied. Rise in temperature caused a corresponding increase in liquid yield for the most part. When less *khat* was used in the feed, however, the percentage yield of liquid product showed a significant decrease as the pyrolysis temperature increased. The release of gases due to favored cracking of plastics as the temperature increased was found to be the main cause for this as well as the most plausible. According to consulted literatures such as (Samolada et al., 1990), longer and heavier molecules, and liquid converted into smaller molecules as the temperature increased. Furthermore, increased formation of alkanes (mainly CH_4 and C_2H_6) with rising temperature was particularly reported along with a notable decrease in the CO and CO_2 content of the gas product (Paradela et al., 2008).

Percentage composition of *khat* had a relatively more profound effect on liquid yield. As the pyrolysis feed contained more *khat*, liquid yield generally increased (Figure 4-3 below). When the feed was pyrolyzed at $550^{O}C$, however, the maximum yield was obtained when HDPE dominated the mixture. A decrease in yield was observed at this temperature when the mixture contained 30% and 0% HDPE. Figure 4-3 below shows the percentage yield plotted against amount of *khat* used for pyrolysis at the different temperatures.

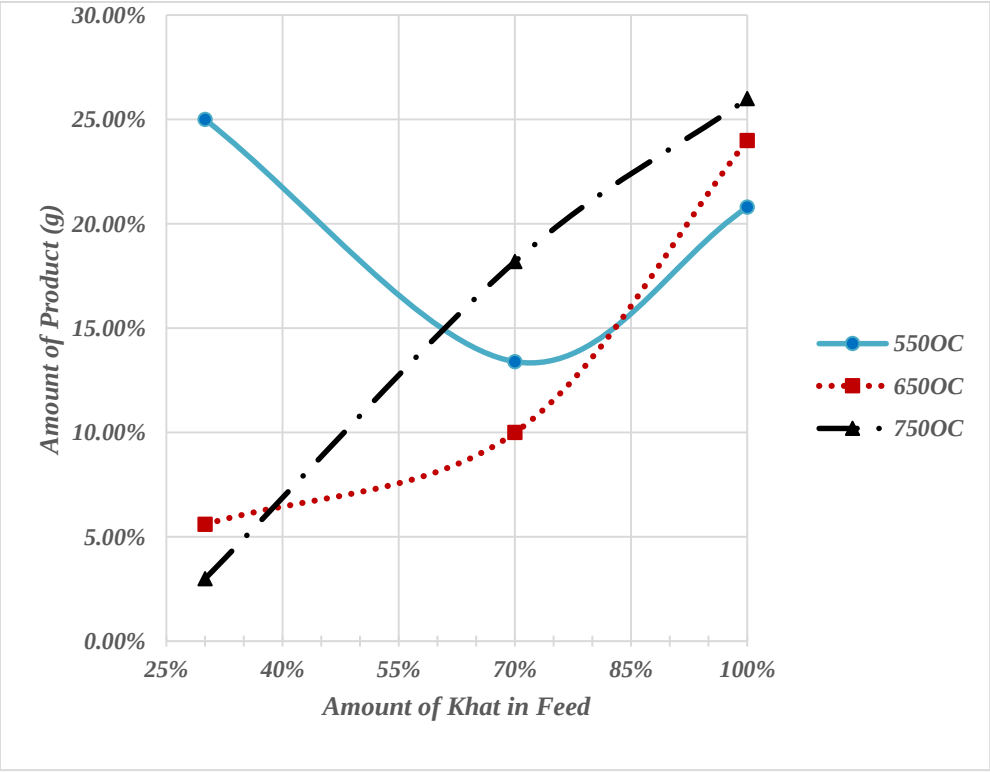


Figure 4-3 – Effect of Waste Composition on Liquid Yield (t = 60 min)

It was concluded that the amount of liquid product obtained by pyrolyzing *khat* and HDPE waste mixture generally gave less liquid yield than solid and gas. The presence of plastic species in the feedstock was not advantageous in terms of increasing liquid yield as anticipated.

At temperatures higher than 300^{O}C, tar and volatile products from pyrolysis of cellulose will undergo further decomposition. According to Sadaka, pyrolysis of cellulose is essentially complete above 600°C and thermal decomposition of tar and some liquid fractions begin leading to the prevalence of gas in the product spectrum (Sadaka, 2008). Therefore, *khat*'s comparatively higher contents of cellulose (59%) and lignin (31.7%) were the main factors that caused liquid yields to remain below 25% at all pyrolysis runs.

In addition, decomposition of *khat* and HDPE materials in a mixture may have lacked synergy to give increased liquid yield. According to several studies on co-pyrolysis, the liquid medium that forms more readily from plastics pyrolysis led to the expectation of improved liquid production due to addition of plastics in the pyrolysis mixture (Paradela et al., 2008) (Pinthong, 2009). This phenomenon was attributed to enhanced heat and mass transfers to consequently facilitate biomass pyrolysis reactions. The presence of plastics, on the other hand, might also improve fuel behavior of liquid products and other properties.

4.5.3 Statistical Analysis

Results from the statistical analysis of experimental data showed that amount of *khat* had the strongest effect on liquid yield whereas pyrolysis temperature had less influence. Effect of

Response Yield

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	921.75	5	184.35	14.11	0.0001	significant
A-Khat Comp.	*439.23*	*1*	*439.23*	*33.61*	*< 0.0001*	
B-T	*53.15*	*1*	*53.15*	*4.07*	*0.0667*	
AB	*337.19*	*1*	*337.19*	*25.80*	*0.0003*	
A^2	*54.81*	*1*	*54.81*	*4.19*	*0.0631*	
B^2	*73.96*	*1*	*73.96*	*5.66*	*0.0348*	
Residual	156.83	12	13.07			
Lack of Fit	*155.85*	*11*	*14.17*	*14.46*	*0.2026*	*not significant*
Pure Error	*0.98*	*1*	*0.98*			
Cor Total	1078.58	17				

Figure 4-4 – ANOVA and Model Fitting Results' Summary

pyrolysis time was concluded to have been insignificant from ANOVA and model fitting results.

Quadratic model (reduced) was selected according to analysis results which showed significance of the model (P-value = 0.0001 for α = 0.01). F-Distribution Test for significance of model and factor effects dictated that the null hypothesis must be rejected if $F_0 > F_{\alpha,\nu_1,\nu_2}$; where v_1 and v_2 are the numerator and denominator degrees of freedom, respectively (Montgomery, 2009). Calculated F-Value for the model was $F_0 = 14.11$ whereas from table we had $F_{0.01,5,12} = 5.06$ which confirmed the rejection of the null hypothesis. Software-generated ANOVA results showing respective F-values and other parameters are given in Figure 4-4 (see above). Other complementary information for statistical analysis of the experimental data that used reduced quadratic model are given in the appendix.

The Model F-value of 14.11 shown in the ANOVA and model fitting results implied a significant model with only a 0.01% (α) chance that a value occured due to noise. In addition Values of "Prob > F" less than 0.0500 indicated model-significant terms while those greater than 0.1000 indicated that the terms were not significant. The lack of fit F-value of 14.46 implied the desirable insignificance of lack of fit. (*See Figure 4-4 above*)

4.6 Characteristics of Liquid Product

The liquid product obtained had a dark-brownish color having a “smoky” and pungent smell – especially when the feed contained more *khat* than HDPE.

Sample from product of Run #1 which was carried out at 100% *khat*, 750^{O}C, and 60 minutes was selected for characterization as it gave the maximum percentage yield.

The density was measured to be 1.1 g/cm^3 while it had a viscosity of 25.6 cp. These values were similar to specific figures and/or range of values reported in several literatures (Czernik, 2002) (Sadaka, 2008) (Sadaka & Boateng, 2009) (Xu, et al., 2011). The very low viscosity was attributed to the probable high moisture content of the bio-oil.

The HHV and LHV, on the other hand, could not be determined using the bomb calorimeter. High moisture content in the sample and improper functioning of the equipment were suspected as possible reasons. However, it was given in works like (Sadaka, 2008), (Sadaka & Boateng, 2009), and others that the elemental composition of bio-oil from pyrolysis is similar to that of the parent biomass. The equations shown below given by (Xu, et al., 2011, p. 207) were hence

used to calculate the HHV and LHV of the selected sample (which was from 100% *khat*) using the elemental composition of *khat* waste. *(See equations 3.15 and 3.16 in section 3.2.4.4)*

$$HHV\ (kJ/kg) = 338.2(\%C) + 1442.8\left(\%H - \frac{\%O}{8}\right)$$

$$LHV\ (kJ/kg) = HHV - 218.3(\%H)$$

where from the elemental analysis results we had: %C = 47.12; %H = 6; and %O = 45.65 (See Table 4-1 on page 43)

Therefore, the HHV and LHV values of the liquid product from pyrolysis of *khat* waste at 750^{O}C were calculated to be 16.36 MJ/kg and 15.05 MJ/kg, respectively.

It was reported by (Bridgwater, et al., 1999) that HHV values of bio-oil from pyrolysis of biomass lay between 15 – 20 MJ/kg. These results were also compared with those of (Pinthong, 2009) who gave the HHV of bio-oil from non-catalytic pyrolysis of rice husk as 4.26 MJ/kg. It was thus indicated that pyrolysis of *khat* gave liquid product with better energy content.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study and analysis showed that *khat* waste can be used in pyrolysis, solely and in a mixture with waste HDPE, to yield liquid fuel. A maximum of 26%.wt of liquid yield was achieved. It was seen that pyrolyzing *khat* waste alone and in higher percentages gave better results.

Proximate, chemical, physical, and ultimate compositions of *khat* waste were determined. These analysis hence made characteristics data available for use as reference in future scientific studies.

It was concluded that *khat* waste is suitable for application in a thermochemical conversion process because of the prevalence of its organic constituents affirmed by its low ash content (5.31% wt. dry basis). Results from chemical analysis (59% cellulose and 31.7% lignin) confirmed the less amount of liquid and correspondingly higher gas product and increased solid formation from pyrolysis at temperatures > 300^{O}C. Elemental analysis, on the other hand, showed the absence of S in *khat* waste. Therefore, using *khat* waste in thermochemical conversion process will not have any risk of significant SO_x emission.

All pyrolysis runs gave a dark brownish liquid that had smoky odor. The average percentage yield for liquid products obtained was 15.57%. The mixture that contained 30% *khat* and 70% HDPE at 750^{O}C gave the minimum percentage yield (3%) whereas the maximum (26%) was from pyrolysis of 100% *khat* at the same temperature. Variation in the total pyrolysis time between 30 and 60 min did not have any significant effect on liquid yield.

Increase in the percentage content of *khat* increased the liquid yield at the cost of increased pyrolysis temperature. Lower amount of *khat* in the feed composition led to higher yield at the lowest temperature studied (550^{O}C). However, pyrolysis at 650^{O}C and 750^{O}C showed corresponding increase in yield as the amount of *khat* became higher. This was attributed to the lower degradation temperature of HDPE which resulted in continual decomposition of liquid produced as the temperature raised to give increased amount of gas product. As respective decomposition of its lignocellulosic components took place at higher temperatures (> 300^{O}C for cellulose, and > 500^{O}C for lignin), more amount of *khat* in the feed led to increased amount of liquid yield.

Pyrolysis of different compositions at the same temperature showed increase in yield as the feed contained more *khat*. Pyrolysis of the same composition at different temperatures, on the other hand, showed a trend in liquid yield that was relatively unclear to explain without the consideration of how much *khat* was present. These two factors were hence seen to have influenced the process rather conjointly.

The HHV of liquid product from pyrolysis of 100% *khat* was calculated using elemental analysis results of dried *khat* waste sample. The rationale for this was the similarity (as given in literatures) between elemental composition of bio-oil from pyrolysis and the parent biomass. Therefore, the HHV of liquid product was calculated to be 17.1 MJ/kg while the LHV was 15.05 MJ/kg

Mixing biomass (*khat*) with a plastic material (HDPE) to use in pyrolysis was aimed at improving the yield of liquid that would have been obtained from pyrolysis of biomass alone. Higher heat and mass transfer rates due to the liquid phase that formed more readily from plastic pyrolysis were anticipated to achieve this. However, this expected enhancement was not observed as even the maximum percentage yield for liquid product was from pyrolysis of *khat* waste alone.

Nevertheless, it would not be correct to conclude that addition of plastic does not bring any benefit. This is solely because only percentage yields but not qualities of liquid produced with and without HDPE in the feed were compared. Lack of qualitative characterization of liquid produced in the presence and absence of HDPE did not allow to make a complete conclusion in this regard.

The application of *khat* waste in a conversion process to recover higher-valued products was investigated in this study. The possibility of managing this waste component, which is generated locally in significant amount, for the protection of the environment and recovery of valuable products was hence demonstrated. Characterization of *khat* waste in terms of proximate, ultimate, and elemental analysis results that produced invaluable information for scientific applications was also substantial.

5.2 Recommendations

Given the demonstrated possibility of obtaining pyrolysis products from *khat* waste, further works are still necessary. Future researches that would be complementary to the present study

aiming at investigation of the process are, therefore, strongly recommended to put due focus on the following points:

- Identification of components present in liquid fuel produced need to be included in future studies. GC/MS analysis will achieve this to enable desired investigation concerning quality of liquid fuel products.
- The conclusion regarding the inclusion of plastic materials shall be made concrete following comprehensive qualitative analysis (such as GC/MS) which needs to also include comparison between samples of fuel produced with and without the presence of plastic material.
- Future works in the area of this and other similar processes must give due consideration to put adequate budget that will assure comprehensive laboratory facility for complete investigation of the process.
- Analysis of the bio-char needs to be conducted in order to identify its applicability to meet any other objectives. Accordingly, respective potentials of bio-char from *khat* waste pyrolysis to be used for carbon sequestration; soil amendment; as heavy metals' adsorbent from wastewaters; or, in general, as a replacement or alternative for other biomass energy systems need to be studied further.
- Production of bio-oil from pyrolysis mostly requires further upgrading and separation processes to improve its properties and remove unwanted components. Numerous researches on pyrolysis of biomass and plastics (both separately and in a mix) reported the invaluable importance of catalysis in the process. Several researches have studied the catalysis effects from zeolites (eg. HZSM-5), transition metals (eg. Zn, and Ni), clay (eg. kaolin clay), and sand (eg, white silica sand). Improvements in distribution and quality of bio-char, bio-oil and gas products were commonly reported. Hence, the effect of catalysis on pyrolysis of *khat* should be investigated so as to develop a complete study concerning possible upgrading from application of catalysts.
- Including such upgrading process in future pyrolysis studies on *khat* or any other biomass is, therefore, strongly suggested to enable production of higher quality liquid fuel. Although, there are many other recent and effective techniques in addition to catalysis, successful incorporation of distillation, solvent extraction, emulsification, or column

chromatography were foreseen given the facilities' limitations that prevail among national institutions within the Ethiopian context.

- Thermogravimetric analysis (TGA) is the most common technique used to study the kinetics and thermal events involved in pyrolysis of solid raw materials. The measurement of weight loss as a function of temperature and time provided by TGA gives good and reliable information. Co-pyrolysis of waste components such as biomass and plastics were also widely investigated using this method. Therefore, future works that aim at studying the pyrolysis of *khat* and plastic waste mixture would rather employ TGA. This way it would be possible to fully investigate the thermochemical conversion behavior of the mixture and determine any synergy among the components and analyze the effects,
- Collection of gas product must also be sought after. It will enable characterization and analysis to identify the presence of high-valued components. Other substantial information such as the amount of GHGs would also be available to lead to corresponding conclusions from another perspective i.e. the issue of climate change.
- In addition to providing energy from a renewable source, bio-oils were also found to contain other non-fuel components. Researches have actually shown the potential of using some of such components in unique applications that may have higher value than fuel. A number of high-value co-products in bio-oils were also identified. Application as adhesive (the water insoluble fraction); food flavoring products or "liquid smoke"; antioxidants; and steroids are some. Therefore, identification of such non-fuel components in bio-oil produced from *khat* through further research has to be considered. The information obtained thereby could be used to study, among others, the overall economic feasibility of pyrolysis of *khat* and the possibility of additional revenues

BIBLIOGRAPHY

Addis Ababa City Government. (2010, February). Overview of Addis Ababa City Solid Waste Management System. Addis Ababa, Ethiopia: Addis Ababa City Government.

Agblevor, F. A., & Besler-Guran, S. (2002). Fractional Pyrolysis of Biomass for High-Valued Products. *Fuel Chemistry Division Preprints , I*(47), 374-375.

Ahuja, P., Humar, S., & Singh, P. (1999). *Chemical Engineering and Technology*(19), 227-282.

Antal, M., & Varhegyi, G. (1995). *Industrial and Engineering Chemistry Research*(34), 703.

Atadana, F. W. (2010). *Catalytic Pyrolysis of Cellulose, Hemicellulose, and Lignin Model Compounds.* M.Sc. Thesis, Virginia Polytechnic Institute and State University, Blacksburg.

Atlabachew, M., Chandravanshi, B. S., Redi-Abshiro, M., Torto, N., Chigome, S., & Pule, B. O. (2013). Evaluation of the Effect of Various Drying Techniques on the Composition of the Psychoactive Phenylpropylamino Alkaloids of Khat (Catha Edulis Forsk) Chewing Leaves. *Bulletine of Chemical Society of Ethiopia, 27*(3), 347-358.

Baggio, P., Baratieri, M., Fiori, L., Grigiante, M., Avi, D., & Tosi, P. (2009, April 5). Experimental and Modeling Analysis of a Batch Gasification/Pyrolysis Reactor. *Energy Conversion and Management*(50), 1426–1435.

Bajus, M. (2011, February 1). Thermal Cracking of Mixtures of Plastics and Woody Material. *Petroleum & Coal*, 1-7. Retrieved from http:/www.vurup.sk/pc/vol53_2011/issue1/pdf/pc_1_2011_bajus_095.pdf

Begum, S., Rasul, M. G., & Akbar, D. (2012). An Investigation on Thermo Chemical Conversions of Solid Waste for Energy Recovery. *World Academy of Science, Engineering and Technology*(62), 625-630.

Bridgwater, A., Czernik, S., Diebold, J., Meir, D., Oasmaa, A., Peacocke, C., . . . Radlein, D. (1999). *Handbook* (Vol. I). Newbury Berkshire, UK: CPL Press.

Brownsort, P. A. (2009). *Biomass Pyrolysis Processes: Performance Parameters and Their Influence on Biochar System Benefits.* A dissertation presented for the degree of Master of Science , University of Edinburgh, Edinburgh.

Costello, D. (2009). *Solid Waste Converstion Technologies Overview.* HDR Engineering, Inc. Minneapolis: Solid Waste Association of North America.

Cox, G., & Rampes, H. (2003). Adverse Effects of Khat: A Review. *Adv Psychiatr Treatm*(9), 456-463.

Czernik, S. (2002). *Review of Fast Pyrolysis of Biomass.* Presentation, National Renewable Energy Laboratory, Golden.

Danje, S. (2011). *Fast Pyrolysis of Corn Residues for Energy Production.* M.Sc. Thesis, Stellenbosch University, Department of Chemical Engineering, South Africa.

Demirbas, A. (2004). Pyrolysis of Municipal Plastic Wastes for Recovery of Gasoline-Range Hydrocarbons. *Journal of Analytical and Applied Pyrolysis, I*(72), 97-102.

Gao, F. (2010). *Pyrolysis of Waste Plastics into Fuels.* PhD Thesis, University of Canterbury .

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., & Roy, C. (2007, January). Vacuum Pyrolysis of Softwood and Hardwood Biomass: Comparison between Product Yields and Bio-Oil Properties. *Journal of Analytical and Applied Pyrolysis, 78*(1), 104-116.

Jenkins, B. M., & Ebeling, J. M. (1995). Thermochemical Properties of Biomass Fuels: An analysis of 62 kinds of biomass for heat value. *California Agriculture,* 14-16. Retrieved May 22, 2013, from http://ucce.ucdavis.edu/files/repositoryfiles/ca3905p14-62863.pdf

Jones, J. (2011). *Mechanisms of Pyrolysis.* Massey University. Melbourne: New Zealand Biochar Research Center.

Kalix, P., & Braenden, O. (1985). Pharmacological Aspects of the Chewing of Khat Leaves. *Pharmacol Rev*(37), 149-164.

Lemessa, D. (2001). *Celastraceae, Catha edulis, Qat, Khat, Mirra.* Addis Ababa: anthropogen.com. Retrieved February 11, 2013, from anthropogen: http://anthropogen.com/2009/06/22/celastraceae-catha-edulis-khat-mirra/

Linden, Li, J., Henriksson, G., & Gellerstedt, G. (2005). *Biochemistry and Bioengineering*(125), 175-188.

Mayhead, G. J. (2010). *Pyrolysis of Biomass*. Presentation, University of California, Agriculture and Natural Resources, Ukiah. Retrieved 2013

Mohan, D., Pittman, C., & Steele, P. (2006). *Energy and Fuels*(20), 848-889.

Montgomery, D. C. (2009). *Design and Analysis of Experiments.* New York: John Wiley & Sons, Inc.

Nencini, P., & Ahmed, A. (1989). Khat Consumption: A Pharmacological Review. *Drug Alcohol Depend*(23), 19-29.

Paradela, F., Pinto, F., Gulyurtlu, I., Cabrita, I., & Lapa, N. (2008, September 4). Study of Co-Pyrolysis of Biomass and Plastic Wastes. *Clean Technology Environmental Policy*.

Paradela, F., Pinto, F., Ramos, A., Gulyurtlu, I., & Cabrita, I. (2009). Study of the Slow Batch Pyrolysis of Mixtures of Plastics, Tyres, and Forestry Biomass Wastes. *Journal of Analytical and Applied Pyrolysis*(85), 392-398.

Paris, R. (1958). Abyssinian tea (Catha edulis Forssk, Celastraceae). *Bulletin on Narcotics, 006*(2), 29-34. Retrieved from http://www.unodc.org/unodc/en/data-and-analysis/bulletin/bulletin_1958-01-01_2_page007.html

Pereira, H. (1988). *Wood Fiber Sci., 20*(1), 82.

Pinthong, P. (2009). *Co-pyrolysis of Rice Husk, Polyethylene and Polypropylene Mixtures: A Kinetic Study.* M.Sc. Thesis, Kasetsart University, Chemical Engineering.

Prakash, N., & Karunanithi, T. (2008). Kinetic Modeling in Biomass Pyrolysis – A Review. *Journal of Applied Sciences Research, 4*(12), 1627-1636.

Regassa, N., D.Sundaraa, R., & Seboka, B. B. (2011). Challenges and Opportunities in Municipal Solid Waste Management: The Case of Addis Ababa City, Central Ethiopia. *Journal of Human Ecology, III*(33), 179-190.

Richardson, T. L. (2006). "Plastics". In *Microsoft® Student® 2007*. Redmond, WA: Microsoft Corporation.

Riediger, T., & Gerlach, D. (2010). *Processes Description Pyrolysis*. (DGEngineering - Gummersbach - Germany) Retrieved 2013, from DGEngineering: http://www.dgengineering.de/Rotary-Kiln-Processes-Pyrolysis.html

Sadaka, S. (2008). *Pyrolysis.* Retrieved June 13, 2013, from http://bioweb.sungrant.org/NR/rdonlyres/57BCB4D0-1F59-4BC3-A4DD-4B72E9A3DA30/0/Pyrolysis.pdf

Sadaka, S., & Boateng, A. A. (2009). Pyrolysis and Bio-Oil. *Agriculture and Natural Resources*, 1-6.

Samolada, M., Stoicos, T., & Vasalos, I. (1990). An Investigation of the Factors Controlling the Pyrolysis Product Yield of Greek Wood Biomass in a Fluidized Bed. *Journal of Analytical and Applied Pyrolysis*(18), 127-141.

Scheirs, J., & Kaminsky, W. (2006). *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels.* (J. Scheirs, & W. Kaminsky, Eds.) West Sussex: John Wiley & Sons Ltd.

Scott, D. (1999). *Journal of Analytical and Applied Pyrolysis*(51), 23-37.

Serio, M. A., Kroo, E., Wojtowicz, M. A., Suuberg, E. M., & Filburn, T. (2002). *An Improved Pyrolyzer for Solid Waste Resource Recovery in Space.* Society of Automotive Engineers.

Shafizadeh, F. (1992). *Journal of Analytical and Applied Pyrolysis*, 283-305.

Sharypov, V., Marin, N., Beregovtsova, N., Baryshnikov, S., Kuznetsov, B., Cebolla, V., & Weber, J. (2002). Co-Pyrolysis of Wood Biomass and Synthetic Polymer Mixtures. Part I: Influence of Experimental Conditions of the evolution of Solids, Liquids, and Gases. *Journal of Analytical and Applied Pyrolysis*(64), 15-28.

Shiferaw, G. (2013). *Characterization of MSW in Addis Ababa.* Addis Ababa Institute of Technology, School of Chemical and Bio-Engineering. Addis Ababa: Unpublished.

Shimelis, B. (2011). Generation, Composition and Characteristics of Urban Solid Waste in a Major Khat Producing and Marketing Area in Eastern Ethiopia. *International Journal of Environmental Protection, I*(5), 9-16. Retrieved from http://www.ij-ep.org

Sinha, S., Jhalani, A., Ravi, M. R., & Ray, A. (2004). *Modelling of Pyrolysis in Wood: A Review.* Indian Institution of Technology, Department of Mechanical Engineering, New Delhi.

Stat-Ease, Inc. (2007). D-Optimal RSM Tutorial. In I. Stat-Ease, *Design-Expert 7.1. User's Guide.* Minneapolis, MN: Stat-Ease, Inc.

Tewodros, T., Arjan, R., & Fitsum, H. (2008). Household Waste Disposal in Mekelle city, Northern Ethiopia. *Waste Management, 28*(10), 203-212.

The Federal Democratic Republic of Ethiopia, Central Statistical Agency (CSA). (2006-2010). Area and Production of Crops (Private Peasant Holdings, Meher Season). In *Successive Agricultural Sample Survey Reports.* Addis Ababa, Ethiopia: Central Statistics Agency.

Van de Velden, M., Baeyens, J., Brems, A., Janssens, B., & Dewil, R. (2010). *Renewable Energy*(35), 232-242.

Vigouroux, R. Z. (2001). *Pyrolysis of Biomass.* Dissertation, Royal Institute of Technology, Department of Chemical and Engineering Technology, Stockholm.

World Health Organization. (2006). Assessment of khat (Catha edulis Forsk). *34th Meeting of the Expert Committee on Drug Dependence.* WHO.

Xu, Y., Hu, X., Li, W., & Shi, Y. (2011). Preparation and Characterization of Bio-oil from Biomass. In D. S. Shaukat (Ed.), *Progress in Biomass and Bioenergy Production* (pp. 197-222). InTech. Retrieved from http://www.intechopen.com/books/progress-in-biomass-and-bioenergyproduction/

Yaman, S. (2004). *Energy Conversion and Management, 5*(45), 651-671.

Yan, Q., Toghiani, H., Yu, F., Cai, Z., & Zhang, J. (2011). Effects of Pyrolysis Conditions on Yield of Bio-Chars from Pine Chips. *Forest Products Journal, 61*(5), 367-371.

Yi, W., Bai, X., He, F., & Yao, F. (2000). Biomass Liquefaction in a High-Temperature Plasma Jet Flow. *Journal of Shandong Institute of Technology, 14*(1), 9-12.

Yishak, A., & Yohannes, D. (2008). *Selection and Development of Fuel Production Method from Plastic Waste.* B.Sc. final year project, Chemical Engineering, Addis Ababa.

Young, G. C. (2010). *Municipal Solid Waste to Energy Conversion Processes: Economic, Technical, and Renewable Comparisons.* Hoboken, New Jersey, United States of America: John Wiley & Sons, Inc.

Yusuf, M. (2008). *Composting of Khat and Related Materials as Solid Waste Management Option in Awaday Town.* Addis Ababa University, Faculty of Technology, Chemical Engineering. Addis Ababa: unpublished.

Zabaniotou, A. A., & Karabelas, A. J. (1999). The Evritania (Greece) Demonstration Plant of Biomass Pyrolysis. *Biomass and Bioenergy, 16*(6), 431-445.

Zafar, S. (2013). *Articles: Current & Archived Articles and Interviews*. Retrieved 2013, from The Alternative Energy eMagazine: http://www.altenergymag.com/emagazine.php?issue_number=09.02.01&article=pyrolysis

Zheng, J., Zhu, X., Guo, Q., & Zhu, Q. (2006). Thermal Conversion of Rice Husks and Sawdust to Liquid Fuel. *Waste Management, 26*(12), 1430-1435.

APPENDIX

A.1.Experimental Design and Analysis Data

A.1.1. ANOVA Table

Table A-1 – ANOVA Table

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	921.75	5	184.35	14.11	0.0001	significant
A-Khat Comp.	*439.23*	*1*	*439.23*	*33.61*	*< 0.0001*	
B-T	*53.15*	*1*	*53.15*	*4.07*	*0.0667*	
AB	*337.19*	*1*	*337.19*	*25.80*	*0.0003*	
A^2	*54.81*	*1*	*54.81*	*4.19*	*0.0631*	
B^2	*73.96*	*1*	*73.96*	*5.66*	*0.0348*	
Residual	156.83	12	13.07			
Lack of Fit	*155.85*	*11*	*14.17*	*14.46*	*0.2026*	*not significant*
Pure Error	*0.98*	*1*	*0.98*			
Cor Total	1078.58	17				

The Model F-value of 14.11 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, AB, B^2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 14.46 implies the Lack of Fit is not significant relative to the pure error. There is a 20.26% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	3.62	R-Squared	0.8546
Mean	15.57	Adj R-Squared	0.7940
C.V. %	23.22	Pred R-Squared	0.6746
PRESS	350.96	Adeq Precision	11.997

The "Pred R-Squared" of 0.6746 is in reasonable agreement with the "Adj R-Squared" of 0.7940.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 11.997 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	9.86	1	1.94	5.64	14.08	
A-Khat Comp.	6.05	1	1.04	3.78	8.32	1.01
B-T	-2.11	1	1.05	-4.39	0.17	1.00
AB	6.47	1	1.27	3.69	9.25	1.00
A^2	3.79	1	1.85	-0.24	7.83	1.01
B^2	4.30	1	1.81	0.36	8.24	1.00

A.1.2. Diagnostic Plots

Figure A-1 – Standard Error of Design

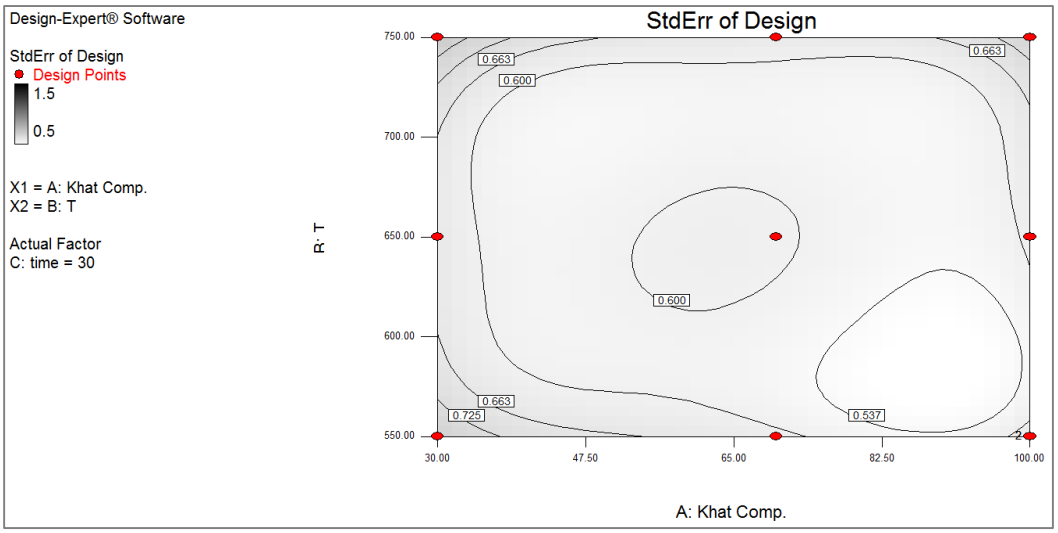


Figure A-2 – Normal Plot of Residuals

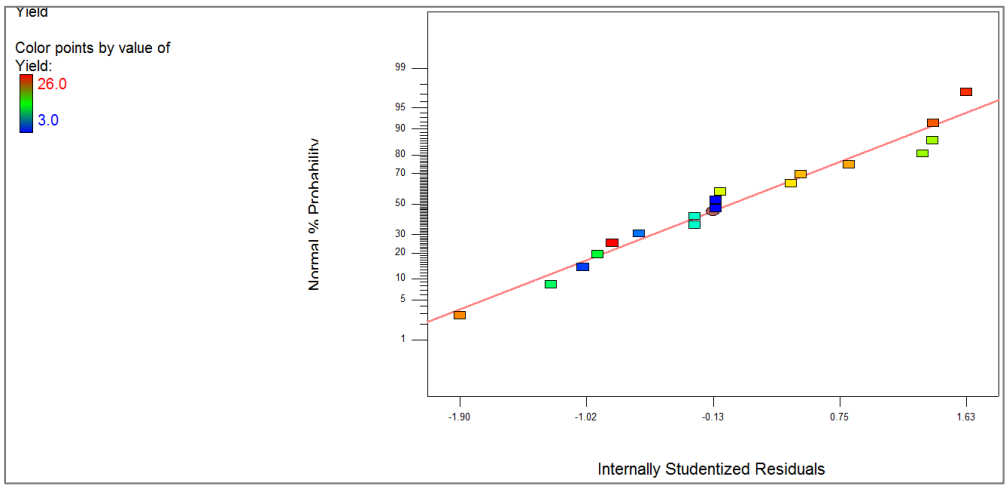


Figure A-3 – Plot of Residuals vs. Predicted Values

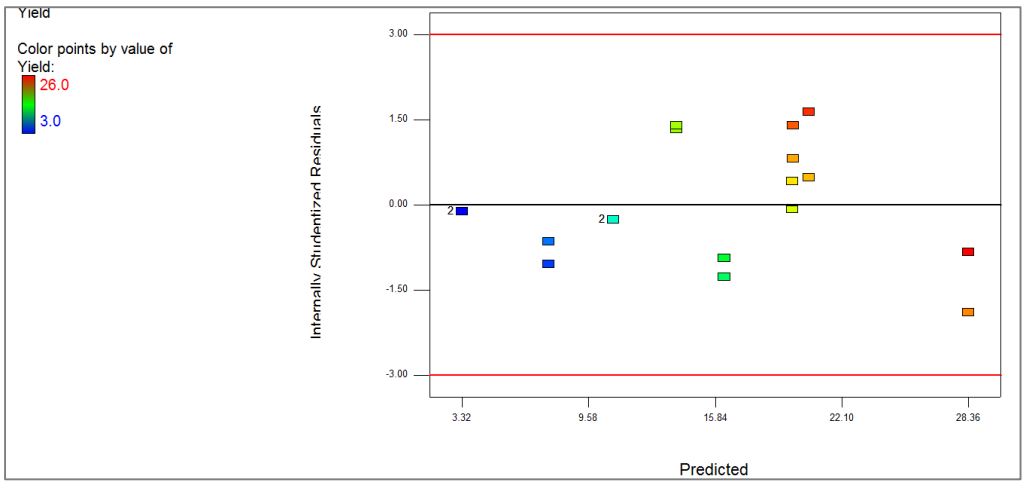


Figure A-4 – Plot of Externally Studentized Residuals

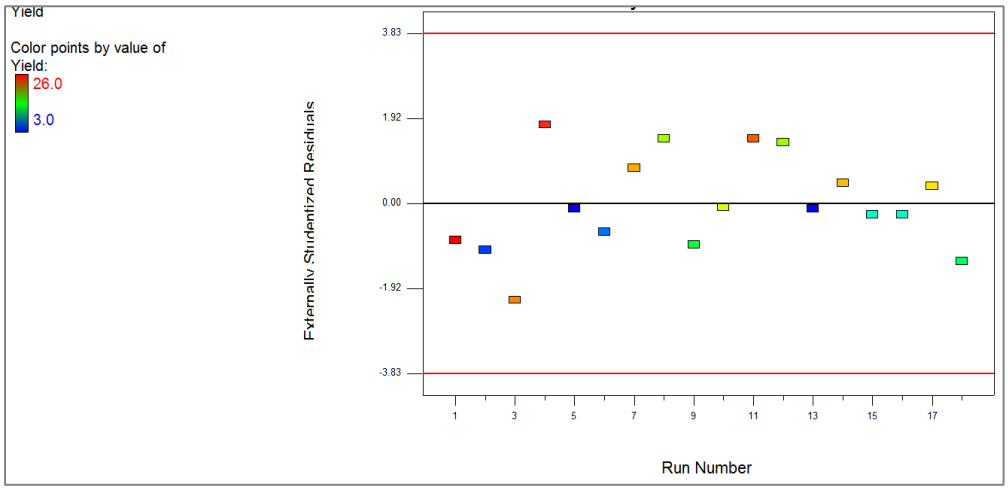


Figure A-5 – Plot of Predicted vs. Actual Percentage Yield Values

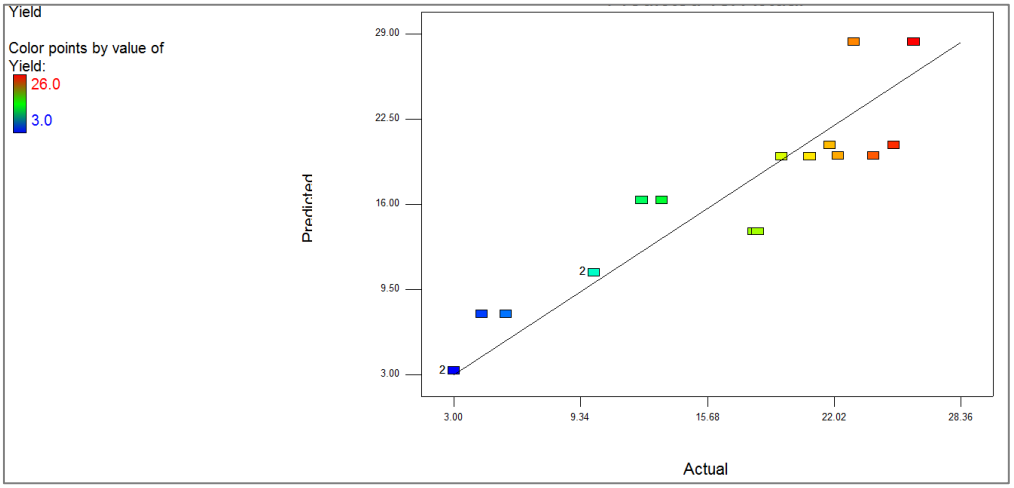


Figure A-6 – Box-Cox Plot for Power Transform

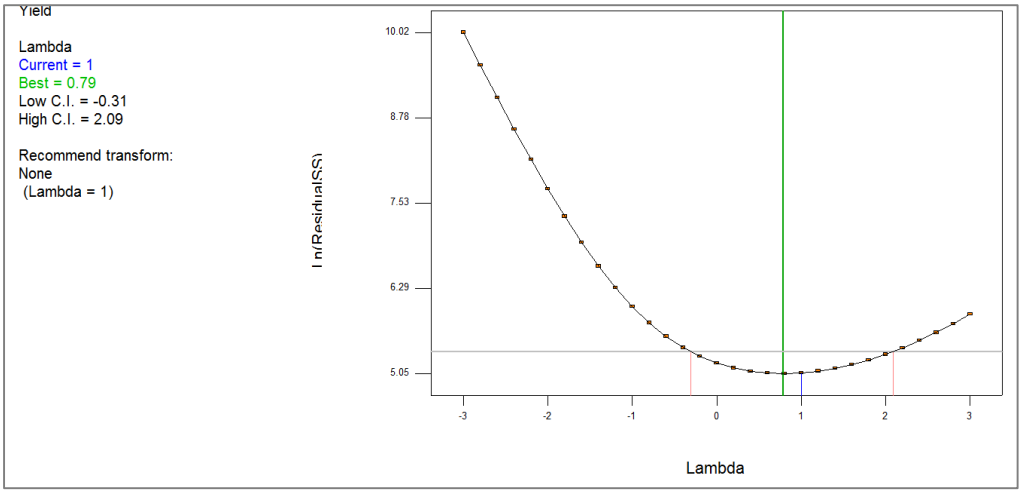


Figure A-7 – Plot of Leverage vs. Run

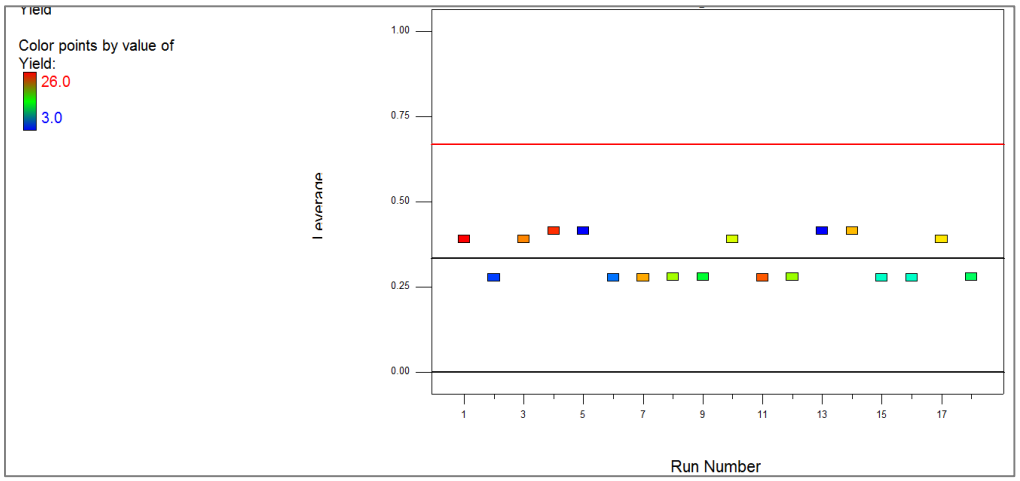
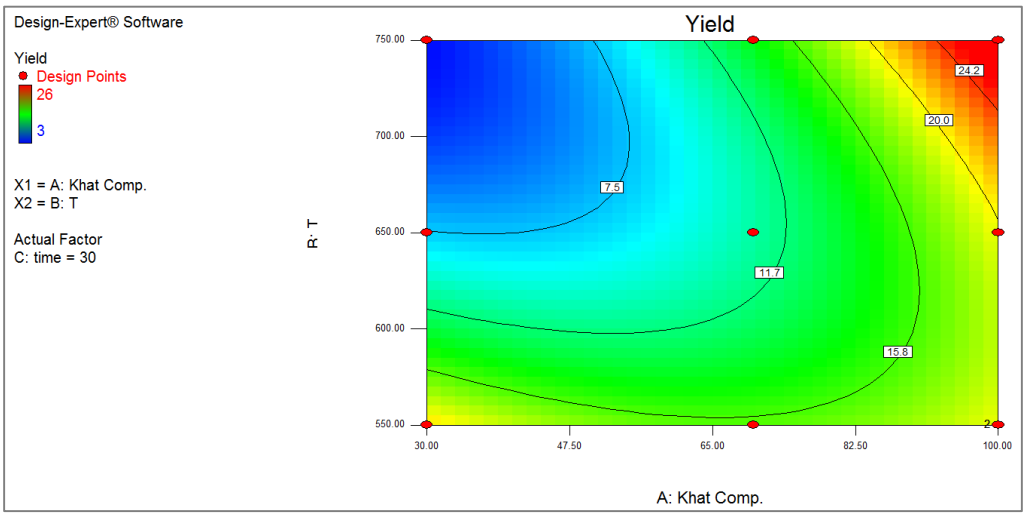


Figure A-8 - Model Graph for Percentage Yield



DECLARATION

By submitting this thesis I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof to the extent where it is explicitly stated otherwise, that reproduction and publication thereof by any party none other than Addis Ababa University's School of Graduate Studies will not infringe any third party rights and that I have not previously submitted it entirely or in part for obtaining any qualification.

	27 FEBRUARY 2014
Signature (Yishak Abdulhafiz Yusuf)	***Date***