SYNGAS PRODUCTION FROM PYROLYSIS OF FURNACE OIL

SUPERVISED BY:

Prof. Dr. -Ing. Naveed Ramzan

Dr. Muhammad Ayoub, UTP Malaysia

SUBMITTED BY:

Aleena Nadeem

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DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF ENGINEERING & TECHNOLOGY, LAHORE

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“All praises to Allah, love for Holy Prophet Muhammad (P.B.U.H) and devotion to Islam”

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I am grateful to my beloved parents who have always provided me moral and emotional support in my life. I am also thankful to my other family members and friends who have supported me along the way.

Abstract

Furnace oil finds a great potential in power generation in Pakistan because refineries are producing it at a large rate. Poor quality fuel burning in power plants is the main cause behind smog. Prime Minister has issued orders for the closure of furnace oil based power plants in order to maximize the consumption of LNG. Due to rapid closure of furnace oil based power plants, refineries are facing storage issues at the plant site. They need to blend it with some other valuable fuel or to sell it at a depressed value in solid fuel market. They are in search of various up-gradation techniques for conversion of furnace oil in to some valuable fuel. In this research thesis, potential of furnace oil in energy production as well as pyrolysis technology, its basic principles and some of the factors that affect pyrolysis products resulting from furnace oil has been studied. Pyrolysis has been employed as a conversion method for furnace oil. Furnace oil has been pyrolyzed under certain conditions and resulted in generation of fuels. The pyrolysis of furnace oil was carried out at various flow rates of N_2 (30-70 ml/min) and temperatures (650-900^{0}C) in a tubular pyrolysis chamber at atmospheric pressure. A critical comparison of pyrolysis parameters followed by resulting product yields and compositions has been made for furnace oil pyrolysis. It was observed that temperature; carrier gas flow rates had profound effects on the conversion of furnace oil as well as product distribution. The maximum gas yield of 65.78% was obtained at 900^{0}C because of high thermal cracking. Higher nitrogen flow rates resulted in high liquid yield because of short residence times of furnace oil in the pyrolysis chamber. It is investigated that furnace oil can produce energy and green chemicals containing negligible amount of sulphur. The recovered syngas from furnace oil mainly consists of hydrogen, carbon monoxide and methane that can be utilized in various applications such as power generation, petro-chemicals, liquid fuel synthesis etc. The recovery of valuable gases from pyrolysis proves to be a better mean for energy security over traditional destructive approaches.

Keywords:

Furnace Oil, Smog, Pyrolysis, Syngas, Energy Security

Table of Contents

List of Tables

List of Figures

CHAPTER 1
Introduction

1.1 Current Energy Scenario

It is predicted that world population will reach around 8 billion in 2025 with existing annual growth rate of 1%.[1] The main share of population evolution will be in developing countries. Urbanization in developing countries like Asia is projected to be greater due to strengthened industrialization resulting in increased energy consumption and waste production. World energy consumption has been increased from 549 quadrillion Btu in 2012 to 629 quadrillion Btu in 2020. It is forecasted that it will further rise to 815 quadrillion Btu in 2040, causing a 48% rise from 2012 to 2040 as shown in figure 1.1.[2] Current global energy supply is based on fossil fuels (coal, natural gas, oil) to a great extent. It is one of the major energy sources but depleting at a fast rate because its reserves are finite. Moreover, its exhaustion results in hazardous gases which contribute to greenhouse emission. According to International Energy Outlook 2016, fossil fuels still contribute major share in energy sector. Among these, Natural gas is quiet the fastest developing fossil fuel in the market. Liquid fuels mainly petroleum based fuels are the largest source of energy supply worldwide. However, liquid energy resources had a fall of 3% in their consumption from 2012 to 2040 as shown in figure 1.2.[2] The reason of this decline is the rapid rise in oil prices, forcing countries to adopt more energy efficient techniques.

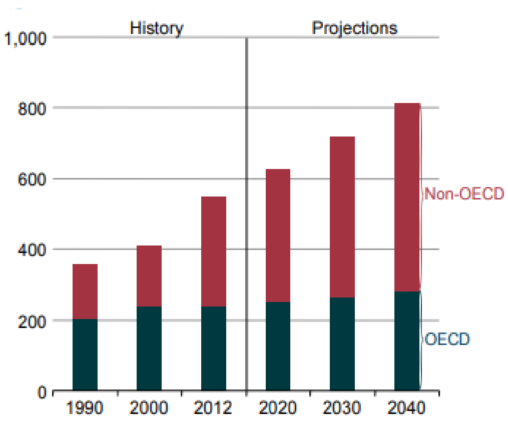
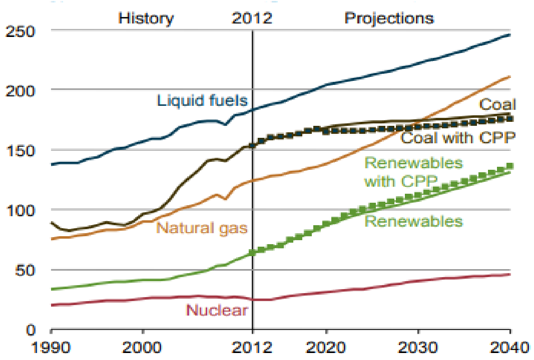


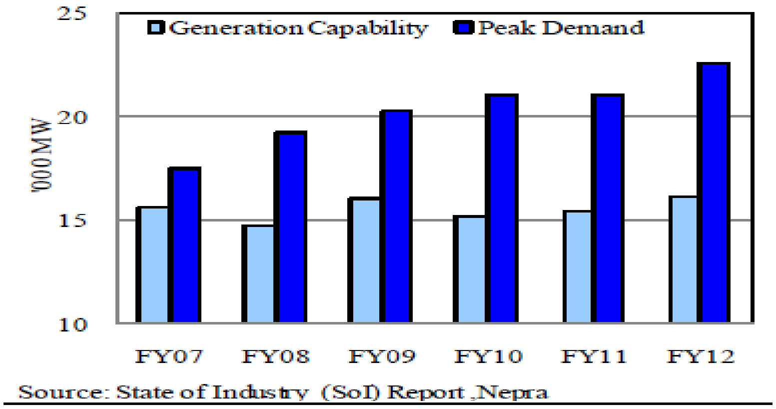
Figure 1.1 Current Energy Scenario, Quadrillion BTU)



Note: Dotted lines for coal and renewables show projected effects of the U.S. Clean Power Plan.

Figure 1.2 World Energy Consumption

Power shortage in Pakistan has become the most hampered economic challenge today. Furnace oil-based electricity production plants which continued as the aspect of Pakistan energy division for over three decades, the decision has been made to be phased out in coming few years. The prediction is that the contribution of furnace oil-based power will decrease from around 35% to an insignificant level in the overall energy mix in the coming years. Power generation capacity of Pakistan industry is quite less than its peak demand as shown in figure 1.3. Facing this prolonged shortage of electricity, consumers have been shifting to alternative renewable sources of power to decrease their reliance on the erratic national power grid. Fossil fuels like coal, crude oil, petroleum and natural gas are producing 13700 TWh of electricity that accounts roughly 84% of the over-all electricity generation as shown in figure 1.4.[3] But these are contributing to greenhouse gases and environmental pollution. With the depletion of fossil fuels resources, increasing temperature, environmental concerns, changing rainfall patterns and raised sea levels, scientific research has been developing in the field of alternative renewable energy sources. Waste to energy engineering has been introduced from recent years as a potential for the production of clean fuels. A renewed interest has been developed related to production of alternative fuels to cope up with the limited energy resources, fossil fuels depletion and constrict emission norms. The technical innovation, process economics, and administrative incentives have made renewable energy division competitive in the energy market. Every year, thousands of people die due to severe heat wave all over the country and if the situation persists, it may lead to catastrophes like acid rain.



Source: State of Industry (SoI) Report ,Nepra

Figure 1.3 Power Shortage in Pakistan

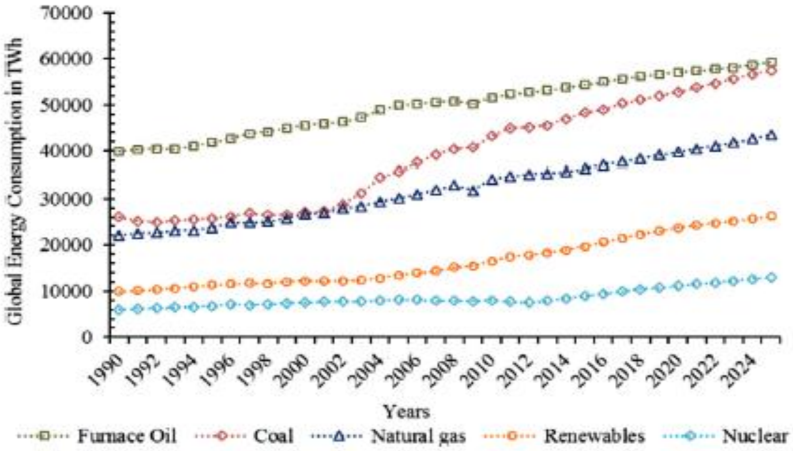


Figure 1.4 Global Energy consumption from furnace oil, coal, natural gas, renewables and nuclear

In 2017; Asian Development Bank encouraged to shift to renewable energy in order to cope with global warming by decreasing greenhouse gas emissions.[4] To fight with these twin crises of fossil fuel exhaustion and ecological degradation, the main focus of the most industrialized and developing countries is to find long-term alternative energy sources which must be ecofriendly. These renewable energy resources like biomass, plastic waste, municipal solid waste and other used oils symbolize a huge under-exploited resource of energy that can easily satisfy much of the rising global energy mandate at prices less than that of conventional fossil fuels if provided acceptable support.

1.2 Furnace Oil

A heavy fuel oil is a dark viscous fuel which is produced as a residue during the blending of mainly heavier components from crude distillation column or a catalytic cracking unit. It is a thick, syrupy, black, tar-like liquid. This fuel is combusted to produce heat and power, as a by-product. Various harmful gasses such as soot, CO, CO_2, NO_x, and O_3 are emitted into the atmosphere if fuel oil is directly combusted, which can lead to smog, depletion of the ozone layer, and drastic temperature variations. Heavy fuel oils contain high sulfur content that is responsible for their combustion to produce large volumes of SOx pollutants that are the real backbone behind the production of acid rain. This can lead to low-temperature corrosion process that is highly discouraged.

Furnace oil based power plants prevails a major share in the generation of power in Pakistan. The Pakistan refineries are producing fuel oil at the rate of 10,000 -12,000 tons/day. It finds wide applications in many areas, including in marine shipping, electricity generation, commercial furnaces and boilers, and in other manufacturing processes.[5]

In 2017, contribution of power generation in Pakistan is almost 34 % from natural gas, 31 % from furnace oil, and 26 % from hydrel, remaining roughly 6 % from nuclear and only 2 % from renewable sources as shown in figure 1.5.

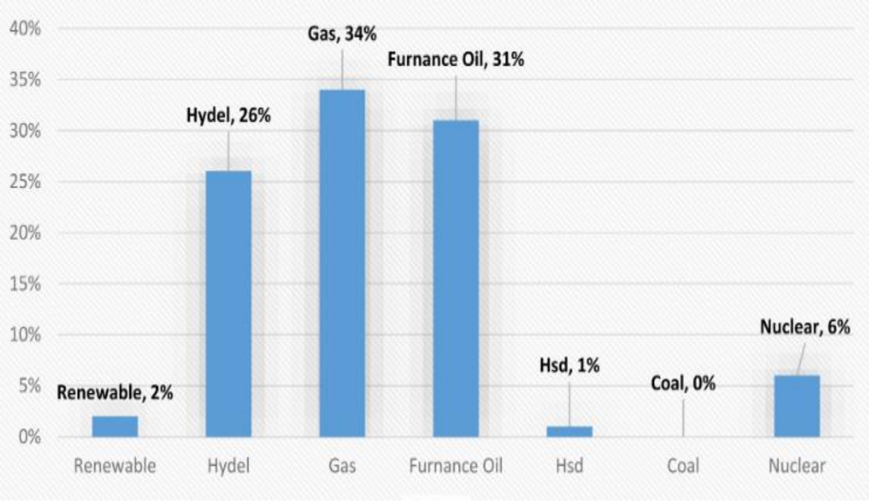


Figure 1.5 Pakistan's Energy Mix

Furnace oil shows a vital role in the international market for liquid fuels because of its low price as compared to other liquids. Though, health and environmental worries related to its high sulfur content have directed novel rules and regulations depicting significantly less prospects for its usage in the future as shown in figure 1.6.[2]

1.3 Effects of Regulations on Furnace Oil Demand

In the past, refinery remains have practiced to sell as sea bunker fuel or used on-site as boiler or furnace fuel. But, with altering regulations, refineries are under force to decrease their emissions and sulfur compounds in their products to make environment friendly so the market for fuel oil is shrinking. To overcome the problem of air pollution and global warming in Pakistan, on October 25, 2017, the Prime Minister of Pakistan has issued orders for closure of fuel oil based power plants so as to facilitate the maximum consumption of LNG.[6] Furthermore; The Ministry of Petroleum and Natural Resources urged to ban the consumption of fuels like diesel, coal and furnace oil for electricity generation in power plants and introduced LNG as the cheapest source of electricity production in Pakistan.[7]

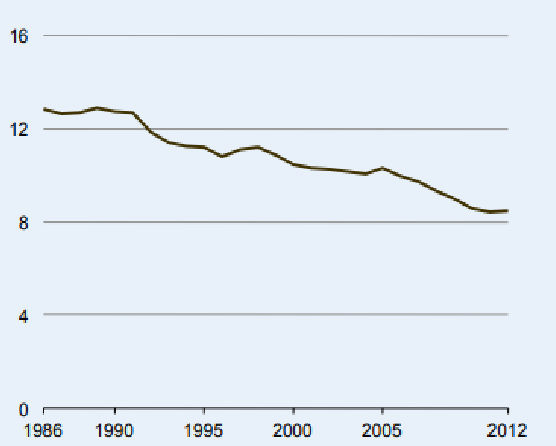
The economics of most refineries are handicapped by relatively high cost of heavy bottom processing. They need to blend it with some valuable product or sell at depressed value in solid fuel market. Therefore, refineries are in search of various ways to upgrade fuel oil so that it can be used as a valuable product. Due to closure of fuel oil based power plants, refineries are facing severe problems of storage of fuel oil at the plant site and the Economic viability of Plant operations.[8]

Pakistan State Oil has reported to the ministry of petroleum that the power plants' consumption is very low and as a result the fuel oil is stored on oil fields and their storages are topped up. Moreover PSO cannot uplift the Heavy and low sulfur containing fuel oil from the Pakistani oil refineries. The officials of oil fields are foreseeing this situation as a leading factor towards complete shutdown of oil refineries. Considering this problematic issue for the production of other products, the government has agreed that some of the furnace oil power plants should start lifting oil from the local refineries so that space for other products could be created on the oil fields.[9]

Byco Refinery (120,000 tons/day capacity) is shutting down its refining complex on the basis of decreased demand of High Sulfur Fuel Oil (HSFO).The refinery is still producing furnace oil and other products at its lowest possible throughput. Similarly the PRL, NRL, Parco refinery Multan and ARL Rawalpindi are in operation but at their lowest possible capacity ranging between 60-70 percent.

Replacement of furnace oil by LNG on abrupt basis will not only effect the production and consumption of furnace oil but it will have a serious impact on the production and export of local crude production from Karachi. The oil companies could not provide the products like high speed diesel, petrol, JP-1 and JP-8 for International Pakistan Air Lines and Pakistan Air Force respectively.[10]

Not only refineries, but ships also contribute a huge share towards pollution, because they use extraordinary sulfur composition in fuel oil. In October 2016, International Maritime Organization (IMO) enforced a new role on sulfur content of marine fuel because burning fuels in ships produce sulfur oxides, responsible for acid rain.[11] IMO has enforced serious regulations for the usage of cleaner fuels starting in 2020.[12] This will open the market for cleaner fuels which will boost demand for efficient cleaning up processes. The problem of consumption of furnace oil could be addressed only if its alternative usage could be introduced. One of the alternatives is to convert the HSFO into clean fuel thereby reducing its heavy emissions. A study in 2016 has showed that the sulfur emission reduction standards will approach levels of no more than 0.5% in 2025 as shown in figure 1.7.[2]



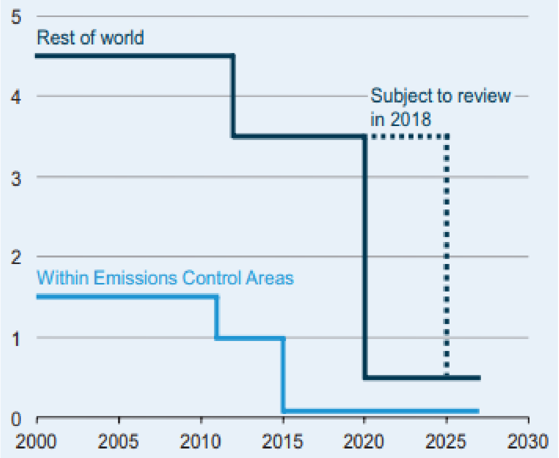


Figure 1.6 World Furnace Oil Consumption(MB/day) Figure 1.7 Regulations on Furnace oil Sulfur content

1.4 Problem Statement

Heavy fuel oils are productive liquid fuel resources for energy production. Ban on the consumption of furnace oil usage in electricity generation has emerged storage problems at plant site in refineries. Also, toxic emission by direct combustion of furnace oil has contributed in global warming. To minimize the bottom product emissions, the refineries are attempting on improving the techniques which are traditionally used to upgrade the fuels.

This research project aims to use an inexpensive technique of high temperature pyrolysis to increase the value of furnace oil by converting it into clean syngas. Pyrolysis is one of the favorable conversion techniques that can resolve most of these problems to a great extent.

1.5 Research Objectives

The specific research objectives are as follows;

- To convert fuel oil into clean syngas resulting in enhanced refinery profitability and resolving the issue of storage, consumption and environmental emissions from heavy furnace oil combustion

- To examine the effect of various process parameters (temperature, nitrogen flow rate) on acid gas production, calorific value and composition of syngas and fuel conversion efficiency

- To perform FTIR spectroscopy, proximate and ultimate analysis for calculating the fuel properties of furnace oil

- Characterization of the pyrolysis gaseous products with the help of gas chromatography

1.6 Furnace Oil Conversion Technologies

A number of thermochemical conversion technologies can be used for conversion of furnace oil to some valuable fuel. Introduction of some of techniques is given below.

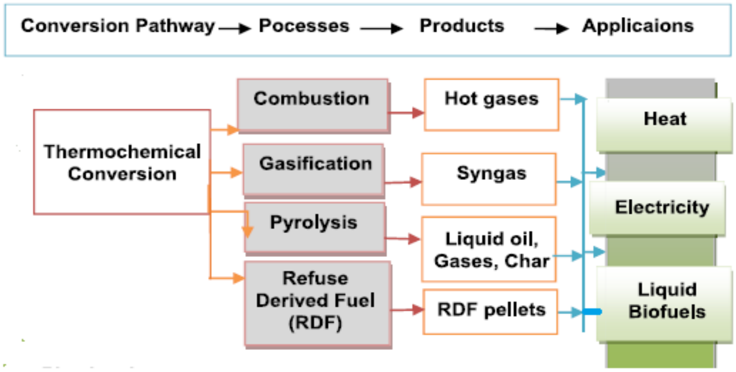


Figure 1.8 Furnace Oil Conversion Technologies

1.6.1 Combustion

Combustion has been using as a waste treatment method worldwide. The process efficiency of combustion is 25-30%. The products of combustion are combustible hot gases mainly consisted of carbon oxides, nitrogen and oxygen. The combustion process gives the benefit of decreasing waste by approximately 80%. Advantages and disadvantages of the combustion process are presented in table 1.

1.6.2 Gasification

Gasification is basically indirect combustion/burning in which thermal cracking reaction occurs in the presence of oxygen. The resulting product is syngas mainly containing CO, CO_2, and H_2 that has potential to be used as a fuel or in electricity generation. Temperature, heating rate and amount of oxygen are the factors that influence gasification process. It is not an environment friendly method because of production of toxic oxidized species in the presence of oxygen.

1.6.3 Pyrolysis

Pyrolysis is a technique that converts heavy feed stock into clean usable gas products. Pyrolysis reduces the average molecular weight of hydrocarbon mixtures by subjecting them to temperatures at which they lose their stability. It is the thermal breakdown of materials at relatively high temperatures in an inert atmosphere which results in the production of a combustible syn gas mainly consisting of H_2, CO, CO_2, CH_4, H_2S, and NH_3. Pyrolysis is a preferred conversion technology than direct combustion and incineration because it consistently shows decreased level of air emissions and also its resulting products are non-corrosive in nature. The amount of sulfur and nitrogen oxides in the resulted product is less so there are no negative effects on human life and environment.

Table 1.1 Furnace Oil Conversion Technologies

Technology	Merits	Demerits
Combustion	Volume reduction up to 80% Can take large quantities of waste Fast treatment	Greenhouse gases leading to air pollution High investment required Large volumes of slag produced
Gasification	Expanded technology Less costly	Toxic oxidized species leading to acid rain High operational and maintenance cost owing to high energy requirement Difficulty of char disposal
Pyrolysis	Recovers up to 80% energy from waste Decreases land requirement Products exhibits high calorific value Plants are easily build	Liquid products gives low yield Coke generation from liquid products

1.7 Pyrolysis Basic Principles

Pyrolysis is a thermo-chemical conversion technology in which material is thermally cracked at elevated temperature in the presence of inert gas such as nitrogen to avoid the introduction of oxygen. The resulted products are gases, oil and solid char. The breakdown of organic materials results in the formation of value added products such as fuels or chemicals in the form of liquid, gas or solid. Long chain hydrocarbons present in the waste material are thermally cracked in to lighter components. It is an endothermic process. Energy input is necessary for the start of reaction. The oil left after pyrolysis is called pyrolysis oil which normally contains tars or phenols. The solid product (char) can be used as a substitute for carbon black. The produced gases find applications as a fuel, household gas or in the production of electricity in power plants.

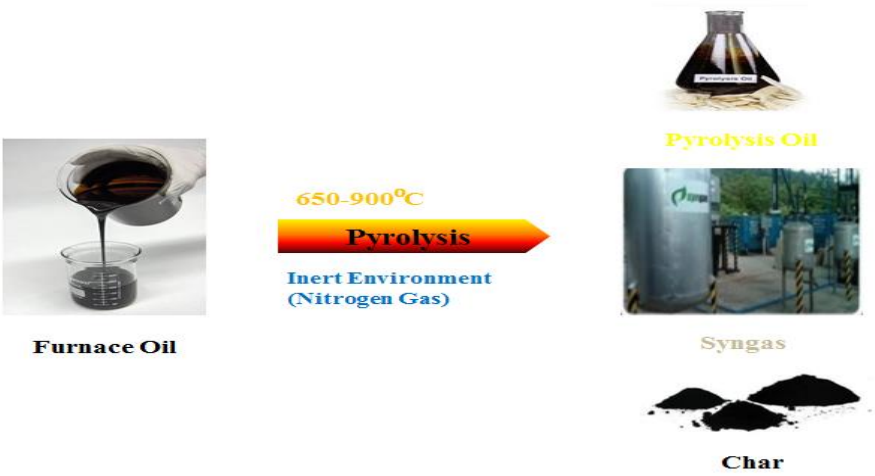


Figure 1.9 Pyrolysis Process

CHAPTER 2

Types of Pyrolysis

2.1 Types of Pyrolysis

Pyrolysis can be categorized into four types on the basis of different operating parameters. The main difference is of the operating temperature, pressure, environment, residence time of the pyrolysed waste in the reactor, heating rate, feed particle size etc. The relative dispersal of pyrolysis products is reliant on on pyrolysis type and pyrolysis working parameters.

2.1.1 Slow Pyrolysis

Slow pyrolysis is usually performed at low temperatures, slow heating rates and for extended residence times. It is a batch process. The residence time in the pyrolysis reactor is 450-550s, heating rate is 0.1-1 with temperature range of 550-950^{0}C. It is favored to increase char production at less temperatures. Since long residence times are involved, a secondary reaction occurs resulting in the cracking of primary pyrolysis products which is not favorable for pyrolysis oil yield and quality. Energy input required is high due to long residence times and low heat transfer.

2.1.2 Fast Pyrolysis

It involves relatively fast heating of waste material at elevated temperature in nitrogen environment with a less residence time. It is a continuous process. The residence time in the pyrolysis reactor is 0.5-10s; heating rate is 10-200 with temperature range of 550-1200^{0}C. On mass basis, it produces majorly 60-75% of oils with 15% char and 20% of gases depending on the feed material used. Further cracking of primary pyrolysis products is prevented by using low residence times. This technology has been proved very effective in the generation of liquid and gaseous fuels because of high heat transfer rates, short residence time in the reactor, fast cooling of gases and précised control of reactor temperature. It requires less investment cost and gives high energy efficiency particularly on small scale.

2.1.3 Flash Pyrolysis

Flash pyrolysis involves residence time less than 0.5s, high heating rate more than 200^{0}C and high reaction temperature of more than 1000^{0}C. It results in the production of up to 75% of pyrolysis oil yield. Rapid de-volatization occurs in an oxygen free environment. The problems encountered in flash pyrolysis are poor thermal stability, solids undesired presence in oil, corrosiveness of oil, increased viscous nature by catalyst enhanced action of char and resulted production of pyrolytic water.

A comparison of operating conditions and resulted product yields obtained from different types of pyrolysis is presented in table 2.1.

Table 2.1 Types of Pyrolysis Process

Pyrolysis Process	**Residence Time (s)**	**Heating Rate (K/s)**	**Temperature (K)**	**Product Yield (%)**		
				Oil	**Gas**	**Char**
Slow	450-550	0.1-1	550-950	30	35	35
Fast	0.5-10	10-200	850-1250	50	30	20
Flash	<0.5	>1000	1050-1300	75	13	12

2.2 Factors affecting Pyrolysis

The factors that affect the yield and quality of pyrolysis products are operating temperature, feed residence time, types of feedstock, type of reactor, presence of catalyst, moisture content, heating rate and carrier gas flow rate. Some of the factors that affect pyrolysis are discussed below.

2.2.1 Residence Time

Residence time of the waste material in the reactor is a main prevailing factor that affects pyrolysis process and it is well-defined according to Mastral et al. (2002) as the average quantity of time that a particle resides in the reactor that may affect product distribution. The rise in residence time may lead to secondary reactions resulting in the formation of unimportant products. Mustafa Balat (2008) observed the variations of the pyrolysis time during pyrolysis of waste engine oil and it was found that the effect of residence time on product yield is minor with a small reduction in oil yield and rise in char yield.[13] The work of Gan and Yaun (2008) on pyrolysis of crop residues stated that increase in residence time had no important effect on gas yield. Char yield decreases drastically with increase in residence time. Ludlow-Palafox and Chase (2001) observed that gase production has increased with residence time in case of plastic pyrolysis. He also concluded that high residence time resulted in primary products conversion into more thermally stable products.

2.2.2 Temperature

The temperature at which the waste material is pyrolysed is very important. The work of T. Valliyappan et al. (2007) on the pyrolysis of glycerol reported that with increase in temperature from 650-800^{0}C, gas and char productio improved considerably with immediate reduction in liquid production. This behavior was owing to high thermal decomposition of the reactant at high temperature. Temperature is also found to have an influence on product gas composition. Production of hydrogen increases whereas that of carbon oxides decreases with increasing temperature.[14]

Weerachanchai et al. (2011) considered the effect of temperature during pyrolysis of palm kernel cake and cassava pulp residue on product yield and observed a sharp decrease in char yield at higher temperatures. Temperature is also found to have an influence on product gas composition.[15]

2.2.3 Heating Rate

The yield of pyrolysis products liquid, gas and char depends on heating rate employed in the reactor. Weerachanchai et al. observed that heating rate in the range of 5-20^{0}C/min had no substantial effect on product yield of pyrolysis of cassava pulp residue. The work of Aida Ben Hassen Trabelsi (2018) on pyrolysis of waste cooking oil showed that heating rate greater than 30^{0}C/min provided higher yields of both liquids and gases and lower yield of char.[16]

2.2.4 Nitrogen Flow rate

The environment in which pyrolysis process occurs also influences the product yield. The work of Munir et al. (2009) on the pyrolysis of different types of biomass under both inert and oxidative environment reported that pyrolysis process behaves thermally different in two different environments. It was concluded that rate of weight loss and reactivity of different types of biomass in inert environment were less than in an oxidizing environment. Isabel Fonts (2012) assessed the consequence of reaction atmosphere change on pyrolysis of sewage sludge in the presence of methane, hydrogen and nitrogen atmosphere. It was concluded that higher liquid yields resulted in hydrogen atmosphere as compared to nitrogen.[16]

2.3 Advantages of Pyrolysis

1. Pyrolysis occurs in oxygen free environment so there are less toxic oxidized species leading to fewer emissions.
2. Pyrolysis has been proved as an environmental friendly disposal method for a number of waste materials.
3. It produces more useful products than standard combustion or incineration.
4. The oil and gaseous products exhibited a high heating value to be used as a fuel. The solid char produced can be used as an alternate for carbon black
5. Pyrolysis plants are easy to build and operate.
6. It does not require as many feed-stock pretreatment steps as compared to other techniques.
7. It reduces carbon footprints by reducing carbon emissions.
8. It involves less difficulty in disposal of sludge and char produced.

2.4 Importance of Syngas

The produced syngas from furnace oil pyrolysis can be used in various applications such as power generation, petro-chemicals, hydrogen and methanol production and liquid fuel synthesis etc. Its current production is still less than the planned production as shown in figure 2.1. The applications of syngas in various sectors are shown in figure 2.2.

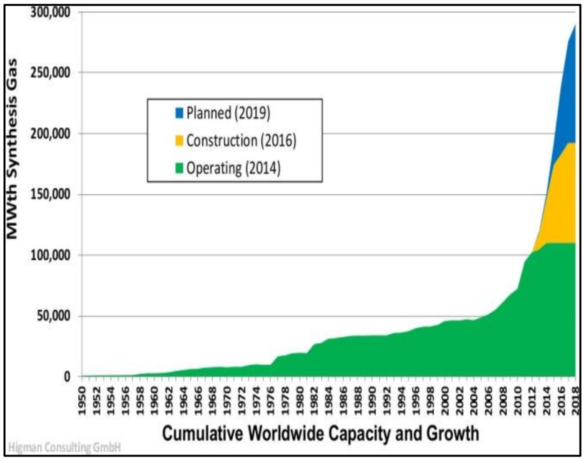


Figure 2.1 Syngas Capacity and Growth

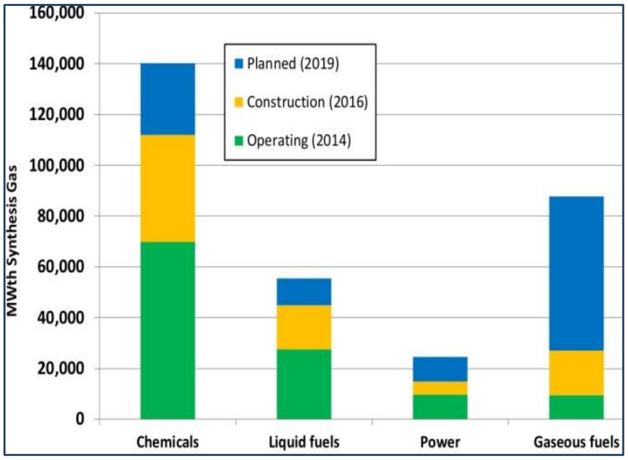


Figure 2.2 Syngas Applications

CHAPTER 3

Literature Survey

A considerable investigation has been conducted on pyrolysis of solids like coal, plastic waste, agricultural waste, and municipal waste from several years. However, there is not so much literature available related to liquids pyrolysis. A restricted number of researches are available on pyrolysis of liquid fuels. Solid waste has been proved as a potential source of energy. A renewed interest has been developed on the conversion of waste solid materials into usable fuels through pyrolysis.

3.1 Pyrolysis of Solid Waste

Syngas generated from pyrolysis of coal exhibits a high calorific value and can be utilize in power generation. Pyrolysis conditions for the removal of toxic pollutants and effect of reaction parameters on syngas yield were optimized.

Dezhen Chen et al. (2015) investigated different pyrolysis techniques for municipal solid waste.[17] The sound effects of temperature, heating rate and residence time on product yield have been examined. In order to solve the problems associated with incineration and landfilling, pyrolysis has been practiced as a safe discarding method for municipal solid waste. Pyrolysis was carried out in fixed bed, rotary kiln, fluidized- bed and tubular reactors. The reported reactors used in the scale-up facilities are rotary kiln and tubular. Rotary kiln reactor has a number of benefits over other types. These include proper mixing of waste material, good thermal efficiency, and adjustable residence time. Tubular reactors are mostly preferred due to their compactness, modular construction, high coke and gas removal efficiency. The products from the commercial plants are reformed syngas as a source of power/heat. Char produced is used as a potential solid fuel.

Petroleum sludge was catalytically cracked and investigation of its pyrolysis products was done by Qunxing Huang et al. (2015).[18] To get rid of emission problems with landfill and incineration of petroleum sludge, energy recovery with the advantage of production of clean products has made pyrolysis a vibrant and promising method. Electrically heated fixed bed reactor made of quartz tube was used to catalytically crack sludge. The produced syngas was characterized using a gas chromatograph. Variations of temperature, nitrogen gas flow rate on syngas yield, gas composition and heating/calorific value and its effects were also studied. Hydrogen yield increased with increase in catalytic temperature.

To combat environmental pollution and biomass management, the focus of research is on thermo-chemical conversion techniques. India is the largest banana producing country in the world with 29.91% share in global market.[19] The banana cultivation corresponds to production of vast quantity of solid waste by virtue of many useless parts of banana. *Musa balbisiana* flower waste obtained from banana fields in India was pyrolysed. The degradation and kinetic behaviors of flower waste were studied at 35-900^{0}C. Valorization studies have indicated that calorific value of the produced fuel from flower waste was comparable to typical biomass.

Energy crops and other agricultural residues such as straw, nutshells and alfalfa stems finds potential in biofuel production. Agricultural Research Service researchers of the USDA considered fast pyrolysis as a best technique for processing switch grass and other wastes. Akwasi A. Boateng et al. (2007) carried out switch grass pyrolysis in a fluidized bed reactor to define energy requirements for endothermic pyrolysis process and product yields that will provide design parameters for scale up plants.[20] Product obtained was consisted of 60.7% bio-oil, 13% char and 11.3% gas.

The antibiotic residue is continuously generated in pharmaceutical industries during antibiotic production processes. These residues may threaten human health if disposed directly to water and soil. Dried antibiotic residues can be regarded as special source of bio-energy because of high organic content present. Pyrolysis of penicillin was performed using thermo-gravimetric technique in Hebei Province, China.[21] Thermal behaviors and product formation mechanisms were discussed. The FTIR spectrum of the resulted product has showed the presence of organic compounds that are inherent in bio-oil.

Disposal of discarded tyres is a big environmental problem because rubber is not biologically degradable. Several recycling techniques, such as retarding, grinding, incineration and reclaiming have been used along the years with certain drawbacks. A renewed interest has been developed on pyrolysis to be practiced as an attractive method for decomposition of wastes. Isabel de Marco Rodriguez et al. and Murena et al. (2001) conducted pyrolysis of waste tyres in an autoclave at 300-700^{0}C. Fixed bed reactor was employed by Laresgoti et al., Berrueco et al., and Williams et al. The effect of pyrolysis conditions on the characteristics of products have been studied by the authors only partially. Tyre pyrolysis liquids are organic and aromatic compounds. Liquid yield increased with increase in temperature from 300-500^{0}C. The similar trend was observed for gases. At lower temperatures, solid char yields are high because of incomplete pyrolysis.[22]

Rapid increase in the demand of rubber gloves in industries is due to awareness about fatal diseases. These used non- biodegradable gloves present many disposal problems. Pyrolysis technology has been intensively investigated for the processing of substances that are associated with biological hazards. William J. Hall et al. (2009) conducted the pyrolysis of latex gloves in a fixed bed reactor loaded with zeolite catalyst at 380^{0}C.[23] The analysis showed that the pyrolysis oil contained dimers, trimmers, tetramers and aromatic compounds in case of un-catalyzed reaction. Due to usage of of zeolite, organic gases were obtained with relatively high yield.

S.L. Wong (2016) made an attempt to study pyrolysis of polyethylene solid waste and then its further optimization by response surface technology.[24] Polymer waste pyrolysis and variations of residence time, system temperature and water-polymer ratio on the liquid product yield of pyrolysis was examined. Reactor temperature was around 350 ^{0}C and pressure was 10 bar.

Efforts were made to determine syngas composition by gas chromatography with different detectors. It was found that gas yield was about 2.6% consisting of hydrogen, methane and other lighter hydrocarbons. The optimum oil production of 13.6% was occurred at 152^{0}C, 1.2 minutes and water- polymer ratio of 32.6.

Energy recovery from plastic waste polypropylene has contributed in plastic waste management. Hydrocarbons production from thermal and catalytic pyrolysis of polypropylene was an effective way of recycling as described by Pramendra Gaurh et al. (2018).[25] A semi-batch reactor was used with nitrogen flow rate of 10mL/min. Temperature range was 500-800 ^{0}C. A critical comparison of pyrolysis parameters has been done in the table 3.1 for various types of solid waste.

Table 3.1 Pyrolysis parameters for various type of solid waste

Sr. No	**Research**	**Pyrolysis Parameters**					**Type of Pyrolysis Reactor**
		Temperature (^{0}C)	**Heating Rate (^{0}C/min)**	**Nitrogen Flow rate (L/min)**	**Feed sample (g)**	**Total Operation Time(min)**	
1	**Municipal Solid Waste**	400-700	10	-	-	40-70	Fixed bed reactor
2	**Microalgae**	450	-	4	20-40	-	Semi continuous cylindrical reactor
3	**Pistachio Shell**	300-700	7	-	-	-	Fixed bed reactor
4	**Petroleum Sludge**	600	10	1	-	-	Quartz tube fixed bed reactor
5	**Polyethylene Solid Waste**	162-338	10	-	20	37-143	Batch parr reactor
6	**Plastic Waste Polypropylene**	500-800	-	0.01	50		Semi batch reactor
7	**Automobile Shredder Residue**	500-750	15	-	166	100	Screw kiln reactor
8	**Tyre Waste**	300-700	5-80	1	175	30	Autoclave
9	**switch grass**	500	-	-	-	-	Fluidized bed reactor
10	**Sugarcane Waste**	700	60	1	30	90	Batch fixed bed reactor
11	**Goat Manure**	300-600	15	0.001	50	30	Fixed bed reactor
12	**Poultry Litter**	450-550	-	18	600	180	Fluidized bed reactor
13	**Cashew Nutshell**[26]	400-600	5	0.05	100	30	Fixed bed reactor
14	**Textile Dyeing sludge**	450-850	-	-	500-700	20-40	Fluidized bed reactor
15	**Pencillin Residue**	327-727	10-30	0.1	10	180	Fixed bed tube furnace

FTIR spectroscopy, ASTM distillation and gas chromatography were used for the analysis of petroleum range hydrocarbon oil. The temperature of 700^0C resulted in high liquid oil productivity of 86%. Gas yield could be increased by increasing temperature resulting in reduced char production. The experimental findings and product analysis has proved thermal pyrolysis a good choice for internal combustion engine fuel production.

Due to industrial growth and rapid economy, the release rate of industrial sludge has been growing from last decades. Globally, portion of water pollution industrially caused by pollutants from textile dyeing is estimated to be 17-20%.[25] Textile dyeing sludge contains toxic organic compounds and its disposal has caused serious environmental problems. Fluidized bed pyrolysis of dyeing sludge was performed and analysis of resulting products was discussed. The pyrolysis oil exhibited sulfur and chlorine containing organic compounds.

The work of David Chiaramonti et al. (2017) on the pyrolysis of microalgae has been proved as a promising pathway for biofuel production. [27] The commercial deployment of microalgae to biofuel conversion on both technical and economic scale is still a major challenge. The conversion process includes cultivation, separation, drying and high temperature pyrolysis. The main products recovered are gases, pyrolysis oil and char. A stainless steel cylindrical reactor, maintained at a temperature of 600 ^{0}C, loaded with 1.5 kg microalgae has produced value added pyrolysis products consisting of 36% of organic phase. Grierson et al. (2009) studied pyrolysis behavior of six species of microalgae for fossil fuel substitution in energy production.[28] Slow pyrolysis was carried out in a micro-reactor and thermal behaviours of species when converted into biofuel, biogas and char were discussed. The process can be made self-sustaining by using the recovered heat of combustible gases as an energy input for pyrolysis.

Previous studies on pyrolysis of coal, oil shale or different biomass samples have shown that pyrolysis temperature is the major factor that affects product yield. Asia has a high rate of cultivation of pistachio and it is increasing year by year. Esin Apaydin-Varol et al. (2007) performed slow pyrolysis of pistachio shell in a stainless steel fixed bed reactor at five different temperatures.[29] The objective was to find the optimum temperature that maximize bio-oil yield. The oil yield increased till 550^0C and a decrease was observed in the range of 550-700^0C.

The poultry farms produces numerous kinds of wastes but the three of principal concern to cultivators are bedding material, manure and dead birds.[30] Past disposal methods employed were land application as a fertilizer and use as an animal feed supplement. Its application as a fertilizer is banned because higher levels of nitrogen and phosphorus can lead to water pollution and eutrophication of lakes. Pyrolysis was performed in a fluidized bed reactor for poultry waste and hardwood, resulting in generation of high value products. Poultry litter bio-oil has more calorific value than that of hardwood bio-oil. Pyrolysis of goat manure was executed in the range of 300-600^0C in a fixed bed reactor[31]. The influence of temperature deviation on product yield was discussed. Maximum yield of gas was obtained at 600^0C. The highest efficiency of produced bio-oil (26%) resulted at 500^0C. The obtained results have identified the presence of organic compounds like hydrocarbons in the bio-oil depicting the potential of goat manure in fuels and useful chemicals generation.

Automobile shredder residue is a problematic waste stream consisting of plastics, glass, rubber and dirt produced by shredding operations during automobile recycling. Pyrolysis can be used as a resource recovery method replacing conventional landfilling. M. Day et al. (1999) conducted experiments on automobile shredder residue in a screw kiln reactor in the range of 500-750^0C.[32] Reactor consisted of a feed zone, reaction zone and product collection zone. Pyrolysis gas analysis indicated that the main components were hydrogen, carbon oxides and lighter hydrocarbons suitable for use as a fuel. Low kiln temperature resulted in high pyrolysis oil production which may need further processing.

3.2 Pyrolysis of Liquid Waste

Pyrolysis of waste liquids has been emerging as an efficient disposal method for various types of waste like motor oil, cooking oil etc. The potential of waste oils in the production of fuel grade chemicals has open the door for renewable energy. Research studies have been extensively attempted to transform solid fossil fuels and other waste materials like coal, tire waste, municipal waste, and used oils into liquid, gaseous fuels and solid char..

Waste engine oil generation is estimated at 24 million tons annually all over the world, posing a major disposal problem for modern age. It presents a cost effective resource for hydrogen production. Kinetic study of waste automobile engine oil was done using thermo-gravimetric analysis at different heating rates in a stirred cylindrical reactor.[33] The sound effects of heating rate on the product distribution and yield have also been considered. The spreading of the liquid products moved a little to smaller carbon numbers in case of decrease in heating rate. A novel technique was used for gaining valued products from the waste lubricating oils. These were sent to a vacuum distillation unit after mixing with crude oil residue. Such a disposal method is no longer feasible because it origins an additional sludge discarding. For that reason, thermal cracking of waste material via pyrolysis needs to be utilized as a best solution from conservational and economic standpoint.[34]

Pyrolysis is applied as recycling method for used lube oil in industry. Waste lube oil was thermally cracked in a batch reactor at temperature range 200-500 °C under vacuum.[35] Variations in temperature have showed straight effect on hydrocarbon oils, gases and char. Resulted gas has a high heating value.

Bio-diesel is a carbon free alternative transportation fuel. A side-product that is obtained during process of bio-diesel production is glycerol. The comprehensive work on its pyrolysis by T. Valliyappan et al. (2007) for the production of safe and cheaper fuels opened the doors for its market. Resulting effects of temperature, nitrogen rate on syngas yield, gas composition and heating value were investigated. Inconel Alloy continuous fixed bed reactor was employed. N_2 gas flow rate was 30-60 mL/min. Temperature range was about 650-800 ^{0}C. The produced syngas consisted of mainly hydrogen, carbon monoxide and small amounts of lighter hydrocarbons. Heating value of syngas was relatively high at 650^{0}C. Among various energetic up-gradation techniques, pyrolysis of glycerol over activated carbons has found commercial outlets such as syngas or value-added liquid chemicals.[36] Two different catalysts (Bituminous carbon and coconut shell) in pyrolysis reactor and two different heating methods (electrical furnace and microwave oven) were used to determine the effect on syngas yield. Pyrolysis was performed in a quartz reactor placed in an inert atmosphere. Carbonaceous catalyst has high selectivity towards hydrogen producing a syngas with a higher H_2/CO ratio. The produced syngas through microwave heating consisted of a higher H_2/CO even at low temperatures. It was concluded that microwave heating is preferred option to be used for up gradation of bio-diesel industrial surplus.

Plant extracts are very crucial biomass sources for the generation of synthetic fuels because these fuels approach the calorific value of hydrocarbons. Pyrolysis was used to produce second generation biofuels from waste cooking oil.[37] Investigation on temperature variations and heating rate effects on bio-oil and gas product yield were discussed. The obtained bio-oil finds applications as chemical feed stocks for active molecules extraction and valorization. It also needs an improvement in its certain properties before its application as an alternative for automobile fuels. The produced gaseous mixture can be used as a fuel for petrol engine, internal combustion engine, diesel engine and for other industrial cracking processes. Fixed bed reactor temperature was 550-800 ^{0}C.

The syngas composition obtained varies depending upon the types of feed stock, pyrolysis parameters and type of reactor. Syngas composition and product yields from various waste is shown in table 3.2.

Table 3.2 Syngas composition from various type of waste

Syngas (%)	**Glycerol**	**Waste Cooking Oil**	**Waste Palm Oil**	**Waste Tyre**	**Coffee Hulls**	**Fish Oil**	**Rice Straw**[38]	**Automobile Shredder Residue**	**Wheat Straw**[38]	**Sugarcane Waste**
H_2	28.9	3	15.04	21.5	25.84	4.76	50.67	53.7	37.1	8
CO	48.7	27	33.49	5.10	20.87	13.43	16.09	5.25	17.5	30
CO_2	1.4	10	44.41	26.2	39.14	11.16	22.56	19.5	20.6	30
CH_4	14.6	12	7.91	17.3	11.8	15.44	7.42	10.1	21.7	27
C_2H_4	4.2	8	2.22	8.70	1.54	22.06	2.01	3.16	0.66	4
C_2H6	1.8	5	0.33	8.20	1.75	8.92	1.05	2.84	0.84	1

Vegetable oils have the dire prospective to be used as a source of fuel in some applications. Residual palm oil cracking was done in a vertical tubular reactor at high temperature.[39] The produced bio-oil was analyzed by GCMS. High grade pyrolysis oil was generated from mixture of palm outer shell and poly-styrene. Pyrolysis was done in a vertical reactor at high temperature and produced syngas was characterized by using FTIR, GC-MS and thermo-gravimetric analysis.

Pyrolysis of used sunflower oil was performed in a fractionating packed bed reactor using sodium carbonate catalyst.[40] The practice of packed column resulted in high residence time, increasing liquid hydrocarbons yield up to 47.3% with a conversion efficiency of 82.7% at 420^{0}C. Process parameters such as temperature, catalyst amount and packed column length have greatly affected product compositions. Liquid hydrocarbons yield is favored at high temperature with a column of small length. Increasing the length of column will result in secondary cracking of pyrolysis products. V.R. Wiggers et al. (2009) performed the pyrolysis of soybean oil in a continuous tubular reactor at 450-600^{0}C.[41] The liquid products were analyzed by gas chromatography. Thermal analysis showed that the produced fuel is of such a calorific value that it can be used for energy production.

Waste frying oil generated from household and hotels was earlier used as animal feed. However, its use has been outlawed because of hazardous effects on the food chain. The disposal of waste frying oil in sewers has disadvantages of odor, energy loss and blockages in sewerage pipelines. Due to global energy growth and the increase in oil prices, researchers are finding ways to use these waste oils as energy source. Takwa Kraiem et al. (2016) examined the pyrolysis of waste frying oil collected from Tunisian fast-food restaurants in a fixed bed reactor at 20-500^{0}C.[42] The pyrolytic oil characterization showed the presence of hydrocarbons, aldehydes, ketones and aromatic compounds. The produced bio-oil has a high liquid yield of 76 wt% and good calorific value 9285 kcal/kg that is close to petroleum based fuels indicating that it can be considered as a worthy fuel.

J.M. Encinar et al. (2009) studied the potential of exhausted olive oil waste in order to minimize the energetic dependence on conventional fossil fuels.[43] The objective was to study yields obtained from both catalytic and non-catalytic pyrolysis of olive oil, performed in two reactors in series. The effect of temperature in the range 400-900^{0}C was observed in non-catalytic and amount of catalyst dolomite 0-100g in catalytic process. Increasing temperature in case of non-catalytic pyrolysis resulted in fall in solid and liquid yield and rise in gas yield. High quantity of dolomite caused a major decrease in the liquid yield and increase in gas yield.

Palm oil waste (palm oil shell, empty fruit bunch) are producing at large rate in Asia especially in Malaysia. Haiping Yang et al. (2006) performed the pyrolysis of palm oil in a fixed bed reactor at a range of temperature 500-900^{0}C.[44] The main products oil, gas and char are in the range of 88.2-95.2%. High temperature is favorable for production of gas products. The effect of catalysts (Nickel, Alumina, Iron oxide) on gas yield was also investigated. Nickel has a pronounced effect giving maximum hydrogen yield. Product yield obtained from different kinds of waste is shown in table 3.3.

Table 3.3 Product yield from various type of waste

Research	Oil	Gas	Char	Research	Oil	Gas	Char
Biomass(Anon n.d.)	75	13	12	**Pine Bark**	30	36	34
Beech(Garcia-Nunez et al. 2017)	9	72	13	**Pinewood Chips**(Westerhof et al. 2012)	12	58	30
Corncob(Pfitzer et al. 2016)	17	62	20	**Pinon-Juniper Wood**	11	59	30
Camphorwood(Pfitzer et al. 2016)	30	50	20	**Poplar Sawdust**	11	77	12
Coffee Hulls	12	63	25	**Plastic Waste**	79	21	0
Douglas Fir wood(Liaw et al. 2013)	40	48	12	**Rice Husk**	13	49	38
Eucalyptus(Heidari et al. 2014)	17	62	26	**Rubber Wood**	19	51	30
Fir Fines(Pfitzer et al. 2016)	22	59	19	**Sewage Sludge**(Sattar et al. 2014)	8	63	29
Fir Pellets	16	62	23	**Scrap Tyre**(De Marco Rodriguez et al. 2001)	38.5	17.8	43.7
Fish Oil(Wiggers, Wisniewski, et al. 2009)	72	15	13	**Softwood**(Henrich et al. 2016)	16	69	15
Glycerol(Valliyappan et al. 2008)	21.5	78.4	0.1	**Sawdust**	30	50	20
Hardwood(Henrich et al. 2016)	18	66	15	**Wheat Bran**(Henrich et al. 2016)	22	60	18
Japanese Cedar	22	66	13	**Wheat Straw**(Pfitzer et al. 2016)	22	50	28
Lemna	28	44	28	**Waste Cooking Oil**(Ben Hassen Trabelsi et al. 2018)	77	20	3
Machinery Oil(Sinağ et al. 2010)	70	25	5	**Waste Cotton Stalk**(Zhao et al. 2010)	14	78	8
Oak(Pfitzer et al. 2016)	30	50	20	**Waste Cotton Stalk**(Zhao et al. 2010)	14	78	8
Olive Stones(Sanginés et al. 2015)	35	38	26	**Waste Olive Oil**(Encinar et al. 2009)	26.5	53.05	20.3

A number of researches have been done on conversion of waste animal fats obtained from food industry including fish waste, beef and poultry waste into some valuable fuel. V.R. Wiggers et al. (2009) conducted experiments on pyrolysis of fish oil collected from waste treatment unit of a fishery industry in Brazil.[49] The product obtained at 525^{0}C was consisted of 73% liquid, 15.85% gas and 11.3 coke. The produced bio-oil is carbon dioxide neutral suitable for energy production. Takwa Kraiem et al. (2015) performed pyrolysis of fish fats waste in a fixed bed reactor at 500^{0}C and analyzed composition of resulting products by GCMS.[50] The liquid yield was 54.6% consisting of bio-oil and organic compounds. Its chemical composition made it a good choice to be used as transportation fuel.

In waste to energy engineering, microwave pyrolysis technology has become popular to add chemical value in waste by producing useful products.[51] Microwave energy as a heat source in pyrolysis was used as disposal method for waste engine oil.[52] Environment unfriendly waste material was thermally cracked to produce clean hydrogen and light hydrocarbons. Yield, conversion and characteristics of the in-condensable gases were discussed. Transformation of waste engine oil into clean gas by using a catalyst bed of carbon particles which is microwave heated resulted in valuable advantages. Pyrolysis was done in a bell-type reactor made of quartz at atmospheric pressure. N_2 flow rate was 0.1-0.75L/min. Feed injection rate was 0.4-5 kg/hr. Temperature range was 250-700 ^{0}C.

Disposal of waste machinery oil is a major environmental challenge. Previously, it was disposed into landfills and drain lines. Ali Sınag et al. (2010) made an attempt to convert waste machinery oil into valuable products.[53] Pyrolysis was carried out in a tubular reactor in an inert environment using nickel as catalyst and the products were analyzed by gas chromatograph. The presence of catalyst resulted in higher thermal cracking giving high gas yield. Mustafa Balat (2008) worked on catalytic pyrolysis of waste engine oil to obtain gasoline and diesel. Perlite and wood ash were used as catalyst. The liquid yield was 92.5% in case of perlite. A critical comparison of pyrolysis parameters has been done in the table 3.4 for various types of liquid waste.

Table 3.4 Pyrolysis parameters for various type of liquid waste

Sr. No	Research	Pyrolysis Parameters					Type of Pyrolysis Reactor
		Temperature (^{0}C)	**Heating Rate (^{0}C/min)**	**Nitrogen Flow rate (mL/min)**	**Feed weight/Flow rate(g)**	**Total Operation Time(min)**	
1	Glycerol	650-800	-	30-70	2.7	30	Inconel fixed bed reactor
2	Waste Cooking Oil	550-800	5-25	-	-	-	Fixed bed reactor
3	Residual Palm Oil	300-700	10	375	0.5	180	Tubular reactor
4	Sunflower Oil	400	40	-	100	180-225	Fractionating column
5	Soybean Oil	450-600	5	-	6000	180	Tubular reactor
6	Waste Frying Oil	20-500	5	0.3	1000	-	Fixed bed reactor
7	Olive Oil	400-900	-	150	10	60	Stainless steel cylindrical reactor
8	Fish Oil	300-700	-	-	9600	187	Continuous Fixed bed reactor
9	Palm Oil	500-900	-	5000	30	30	Counter current Fixed bed reactor
10	Ethanol	700-1200	-	1000	-	180	Quartz reactor
11	Machinery Oil	400-800	5	30	-	60	Tubular reactor

Renewable nature of ethanol makes it a best choice to be used as a fuel and it has ability to reduce soot formation. The pyrolysis of ethanol was studied at variations of temperature from 700 to 1200^{0}C in a quartz reactor.[54] The resulted gas mixtures contained carbon oxides and lighter hydrocarbons. Elemental analysis, X-ray diffraction and other several characterization techniques have been used to characterize soot products.

CHAPTER 4

Materials & Methods

4.1 Materials

- Furnace oil Sample from Byco Refinery
- Water
- Sodium Hydroxide
- Silica Gel
- Ceramic Wool

Furnace oil collected from Byco Refinery is used as a feedstock material. Water and sodium hydroxide are used as cleaning agents in bubblers for gas cleaning. Silica gel acts as drying agent to remove moisture from gas.

4.2 Experimental Setup

A lab scale continuous flow pyrolysis plant has been designed and developed to simulate high temperature pyrolysis. The plant facility carries out electrical pyrolysis/gasification with adjustable fuel residence time and operating conditions to produce consistent quality syngas. The plant has a syngas generation section followed by several syngas cleaning stages. The main parts of the system are feeding structure, nitrogen injection system, pyrolysis chamber and heater, gas/ solid separation, vapors condensation system and instrumentation and control system. Produced volatiles and char leave the pyrolysis chamber at top. The solid char particles are removed from syngas in the char collector.

Syngas is sent to a water cooled condenser where it is condensed to form a pyrolysis liquid/ oil. The separated gas is passed through a series of bubblers and then it is collected through sampling ports in sampling bags for analysis purpose. The plant material of construction is carefully chosen to be of Stainless Steel of various grades to ensure its stability under several process conditions.

4.2.1 Feeding System

The plant can be operated with both solid and liquid feed.

Figure 4.1 (a) Metering Pump (b) Feeding Hopper (c) Feeding Screw

Screw feeding is used because of advantages of simple structure and suitable operation. In case of solid feed, it has a fuel feeding auger which is placed inside chamber. It is joined to a adjustable speed geared motor. To holdup fuel, a hopper with a feeding valve, regulator, and cone is attached to a fuel feeding auger. Whereas, to operate it with liquid feed, Iwaki metering pump of capacity 450 ml/min is used as shown in figures 4.1 a, b and c.

4.2.2 Nitrogen Injection System

A nitrogen cylinder to avoid oxygen entry into the chamber and to assure an inert medium for pyrolysis reactions is connected with a nitrogen purging valve. A pressure gauge is also installed at cylinder for flow regulation. A gasifying agent (air) can be introduced to carry out gasification.

4.2.3 Pyrolysis Chamber and Heating System

The pyrolysis process takes place in a pyrolysis chamber which is tubular. This tubular pyrolysis chamber is surrounded around auger length. PCSIR tube furnace (max 1200^0C) is connected to the chamber. In pyrolysis chamber, an electrically heated tubular heater is placed with a temperature controller. Reaction temperature is measured with the help of a thermocouple. Pyrolysis occurs in the pyrolysis chamber to produce syngas. This heating assembly offers the fast energy input ensuing high heating rate necessary in the pyrolysis reaction. Pyrolysis of furnace oil is conducted at temperature of 650-900°C with inert gas. The gas residence time in the chamber is a key factor to perform pyrolysis for syngas generation. The chamber is designed and fabricated in tubular shape prepared of stainless steel 316 with wall thickness 4 mm, internal diameter of 5 1/2" and length of 10 3/4".

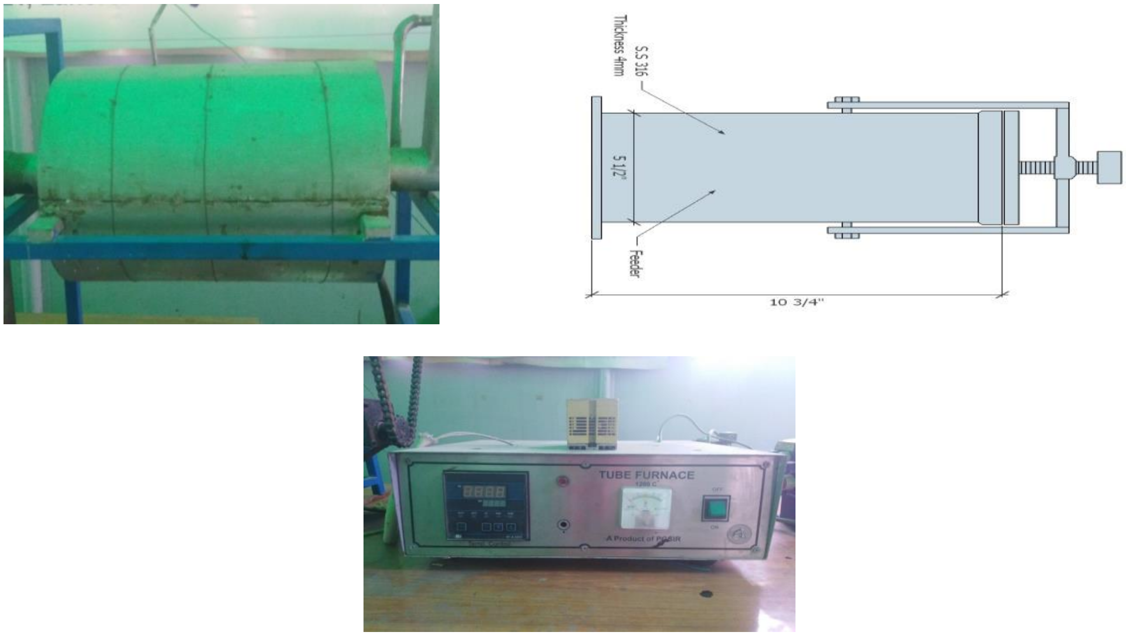


Figure 4.2 Pyrolysis Chamber and Furnace

4.2.4 Gas/ Solid Separation System

Syngas exiting the chamber contains tiny particles like sand, char and ash. These undesired particles from gas are removed in a separate vessel. Char particles are necessary to remove from the syngas due to reason that they can reduce the condensation system performance and efficiency causing obstruction in the condenser tubes. Char is removed in a separate vessel called char collecting vessel. It is made of stainless steel 316 pipe of wall thickness 4 mm, internal diameter of 3 1/2" and length of 11 3/4".

4.2.5 Vapor Condensation System

The condensation of produced vapors discharged from the reactor upsets the yield and quality of the syngas. The shell and tube water condenser is basically designed to assist easy cleaning in order to avoid fouling. The condensers tubes are made of stainless steel because liquid has a corrosive nature.

4.2.6 Syngas Cleaning System

After char/ash collection chamber, there is a syngas clean up train to remove contaminants. Three syngas bubblers B1, B2, B3 remove remaining hydrocarbons and heavy tar with in non-condensable gases using distilled water or caustic solution. A fine ceramic wool tar filter is also connected after bubbling system to trap some light tar. Syngas is then filtered and dried in a filter and desiccant holding chamber containing silica gel F1. Finally, there is a chilled water syngas bubbler B4 to remove tar from gas yielding clean syngas. Syngas contains large number of undesirable components and impurities which are trouble causing in the latter applications. Therefore, its cleaning is necessary.

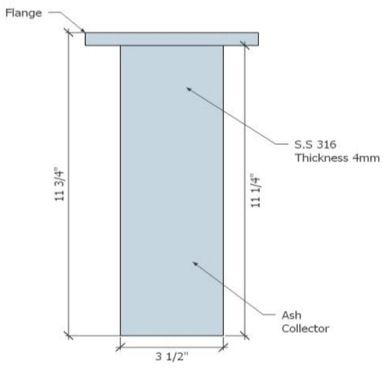


Figure 4.3 Char Collector

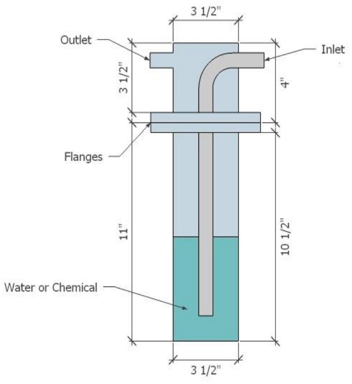


Figure 4.4 Bubbler

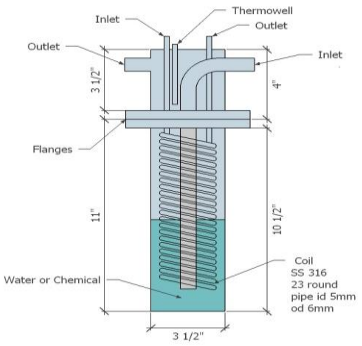


Figure 4.5 Coil Bubbler

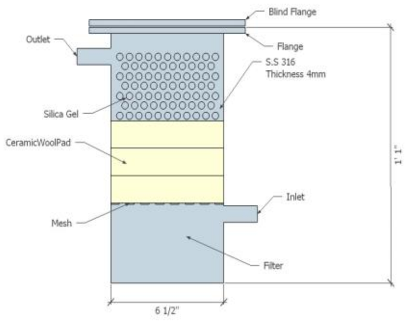


Figure 4.6 Filter and Desiccant Holding Chamber

4.2.7 Instrumentation and Measurement System

Control system of lab scale pyrolysis setup comprises of temperature, pressure, composition and flow measurement. Thermocouple is installed at pyrolysis chamber to measure temperature. The plant contains a number of gas sampling ports so that the chemical composition of cleaned syngas is recorded using an on-line gas analyzer.

Syngas can be directly supplied to light up a burner flame. Rota-meters are provided for both liquid and gas flow measurement. Pressure sensors are installed at outlet of bubblers to indicate gas pressure. Solenoid control pressure safety valves are also placed. The flow rate of nitrogen gas to the chamber is regulated through the needle valve.

A screw feeder is used as a conveyor for solids transport from hopper and feed flow rate is attuned with the velocity of feeder. The temperature of the pyrolysis chamber is controlled by controller using thermocouple as a measuring device.

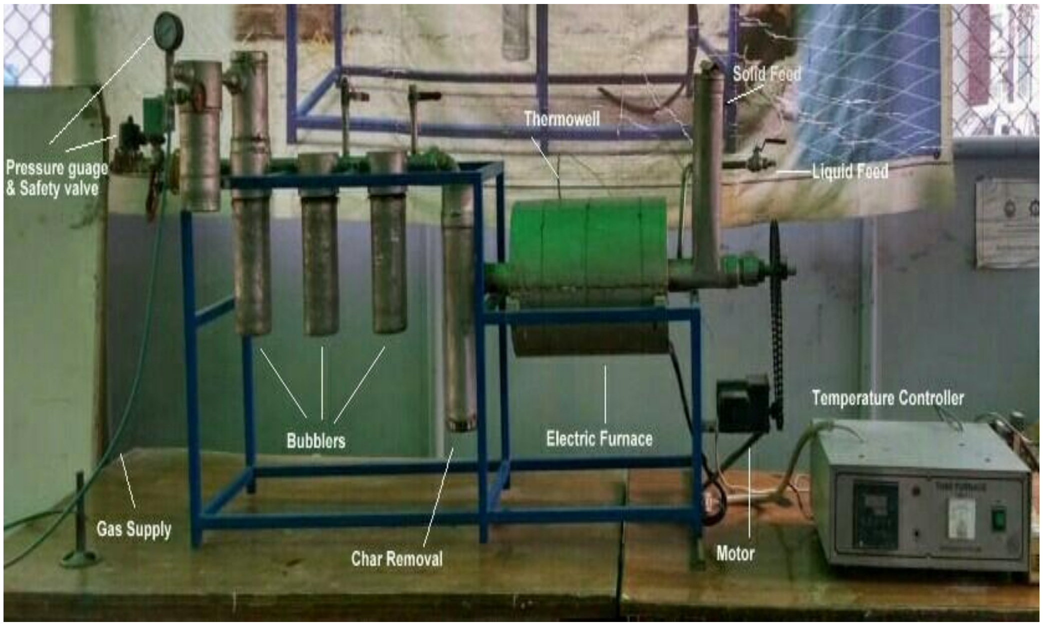


Figure 4.7 Lab Scale Pyrolysis Setup

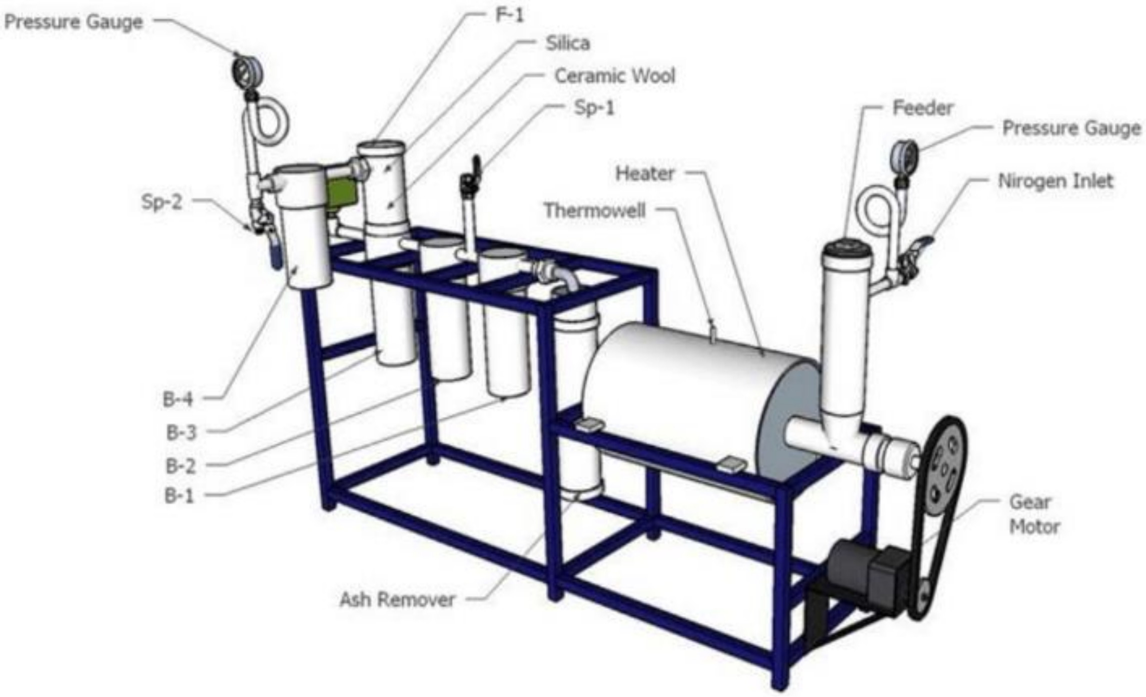


Figure 4.8 3D view of Pyrolysis Plant

4.3 Experimental Procedures

4.3.1 Preheating of Furnace Oil

Furnace oil is highly viscous. Its viscosity affects the amount of pre-heat mandatory for handling, storage and atomization. If furnace oil is highly viscous it results in difficult pumping, burner lighting and operation may be undependable. Poor atomization can cause severe carbon deposits on the burner tips/walls.. Pre-heating of furnace oil up to 50^0C is necessary for proper atomization.

Figure 4.9 Furnace Oil Preheating in Oven

4.3.2 A Typical Run

The desired temperature of pyrolysis chamber was achieved in 20 to 30 minutes. Nitrogen gas was permitted to flow at the desired flow rate of 15 ml/min whereas heating the reactor to the operated temperature. Ceramic wool, water and silica gel were filled in the bubblers. Furnace oil was pumped in to the chamber using a metering pump at the rate of 10 ml/min. The product leaving the chamber was sent in to a char collector where char is removed. Liquid is collected in collection vessel. After gas cleaning, it is collected in a sampling bag.

4.3.3 Gas Sampling

Syngas is collected in gas sampling balloons for analysis by gas chromatograph.

Figure 4.10 Gas Collections in Sampling Bags

CHAPTER 5

Results & Discussions

5.1 Specifications of Furnace Oil

Some physical properties of furnace oil such as density, viscosity, calorific value etc are presented in table 5.1.

Table 5.1 Furnace Oil Properties

Property	Test Method	Specification Limit & Unit	Test Result
Density	D-1296	g/cm^3 0.89-0.95	0.93
Specific Gravity	D-1298	- 0.90-0.98	0.942
Kinematic Viscosity	D-445	cSt max 300	118.5
Pour Point	**D-97**	^{0}C Max 24	15
PH	PH Paper		Neutral
Calorific Value		Kcal/kg	10142

5.2 FTIR Analysis of Furnace Oil

FTIR spectroscopy technique is utilized to recognize the important functional groups in the furnace oil. In the obtained FTIR Spectra, transmittance vs wave number peaks are examined to recognize the functional groups existing in the furnace oil and are presented in the table. Carboxylic acids are found in the medium transmittance peak of O-H of 1723 cm^{-1}. The alkanes are specified by the medium narrow transmittance peaks of C-H vibrations of 1458-1375 cm^{-1}. The aromatic compounds are characterized by presence of the transmittance peak of 747 cm^{-1} wavenumber in 680-860 cm^{-1} range.

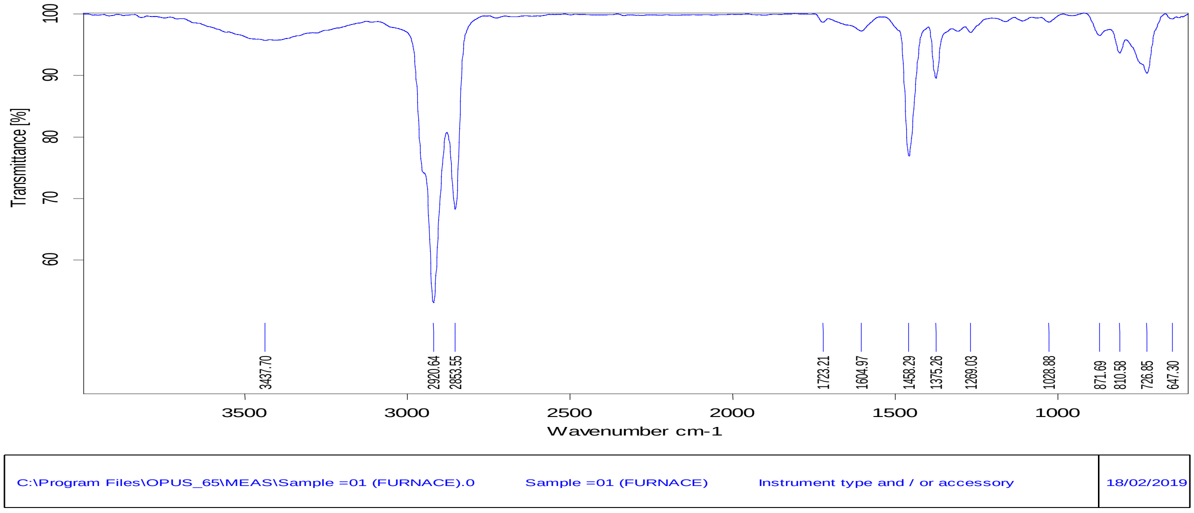


Figure 5.1 FTIR Spectrum of Furnace Oil

Table 5.2 Functional Groups in FTIR Spectrum of Furnace Oil

Wavelength of transmittance (cm^{-1})	**Functional Group**	**Compound Class**
2920.64-2853.55	C-H Stretching	Alkane (-CH_2 and CH_3 of saturate)
1723.21	C=O Stretching	Carbonyl/ Carboxylic groups
1604.97	C=C Stretching	Alkene
1458.29-1375.26	C-H bending	Alkane (methyl/ methylene group)
1269.03	C-N Stretch	Aromatic Amine
1028.88	S=O stretch	Sulfoxide
810.58	C-H Bending	1,4 di-substituted
726.85	C-H Bending	Benzene derivative
647.30	C-Br stretch	Halo compound

5.3 Temperature Profile for Pyrolysis

Before starting feed, first the pyrolysis chamber has to be maintained at the desired pyrolysis temperature. It is achieved by means of furnace and temperature controller. The time required to reach the desired temperature is recorded and then this temperature is kept at a constant value as the process proceeds.

Table 5.3 Time v/s Temperature Data for Pyrolysis

Time (min)	Temperature (^{0}C)
7	85
12	130
14	165
16	225
19	280
21	360
24	425
27	500
30	565
33	630
36	750
40	800
43	800
45	800

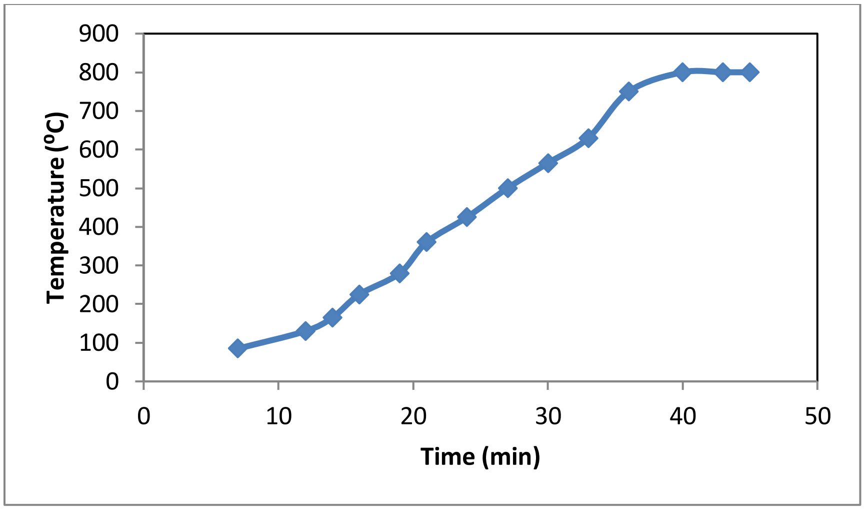


Figure 5.2Temperature Profile for Furnace Oil Pyrolysis

5.4 Test Run Conditions for Pyrolysis

Several test runs were carried out for furnace oil pyrolysis at a range of pyrolysis conditions. Operating conditions for tests 1 to 5 with varying temperatures and nitrogen gas flow rate are shown in table 5.4.

Table 5.4 Test Run Conditions for Furnace Oil Pyrolysis

Test Number	**T1**	**T2**	**T3**	**T4**	**T5**
Temperature, ^{0}C	900	850	800	750	700
Fuel Residence Time, min	2	2	2	3	3
Furnace oil Flow rate, ml/min	10	10	10	10	10
Nitrogen Flow rate, ml/min	30	30	50	50	70

5.5 Calculation of Pyrolysis Product Yields

The pyrolysis product consists of three components such as gas, liquid and solid char collected after each experimental run. The mass of each constituent in the experiment is achieved by weighing the furnace oil feed and product (liquid, gas and char). Total gas yield (wt. %) was experimentally determined by measurement of total gas volume and gas density. Gas volume was measured using gas flow meter (Rota meter). The volume mean density of gas was calculated based on the gas components at stable experimental conditions (normally after 5-10 minutes of sample feeding). The gas weight can be easily determined from its volume and density. The pyrolysis liquid is collected from both bubblers and its weight is determined with weight balance. Solid char is collected from char collector and weighed. According to this method, the sum of gas, liquid and char collected in the experiment is in the range of 85-90 %. The remaining part (15-10 %) may be lost as some in-condensable liquid oil, moisture and fine particles (may be get absorbed on silica gel gas drying column or in quartz wool filter).

5.6 Effect of Operating Parameters on Product Yield, Syngas Composition & Calorific Value

5.6.1 Effect of Pyrolysis Temperature on Product Yields

The effect of temperature on product yield during furnace oil pyrolysis is shown in figure. With increase in temperature from 600-900 ^{0}C, gas yield increases significantly from 40.89 to 65.78 %. The experiment showed that maximum liquid yield of 33.44 % was obtained at 600^{0}C. As soon as temperature started increasing, gas yield go on increasing. At 600^{0}C, gas yield was at minimum. The maximum gas yield of 65.78 % was obtained at highest temperature of 900^{0}C.

Table 5.5 Temperature v/s Product Yield Data for Furnace Oil Pyrolysis

	Temperature (^{0}C)						
Fractions	600	650	700	750	800	850	900
Gas	40.89	44.56	49.98	52.67	57.89	63.98	65.78
Oil	33.44	31.12	27.23	25.36	22.56	20.78	18.23
Char	8.99	9.34	9.89	10.13	11.98	12.56	13.11

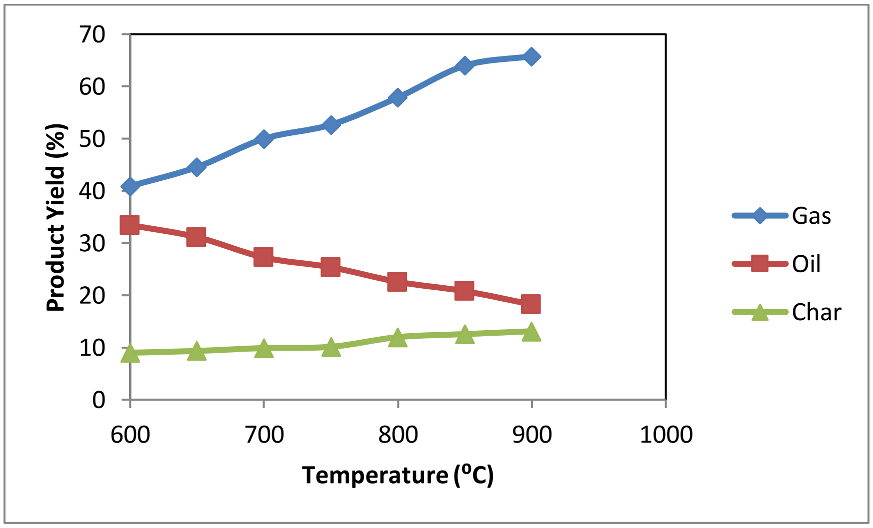


Figure 5.3Temperature v/s Product Yield for Furnace Oil Pyrolysis

Liquid production shows a decreasing trend. Char also shows a modest increase with increasing temperature. The reason is higher degree of thermal cracking and de-volatilization at high temperature.

The results showed that yield of pyrolysis oil is 18-33 % which is low in all the runs whereas yield of char is from 8-13 % and yield of produced gas is 40-66% which is high. These results may be due to secondary cracking reactions as well as the operating conditions of the pyrolysis process.

5.7 Effect of Nitrogen Gas Flow Rate on Product Yields

The effect of nitrogen gas flow rate on product yield resulting from furnace oil pyrolysis is shown in figure. By increasing nitrogen flow rate from 30-70 ml/min, liquid yield has been increased. Whereas, gas and char followed a decreasing trend. The residence time of furnace oil in pyrolysis chamber has been decreased due to increased carrier gas flow rate. Higher flow rates tends to shorten the feed residence time and furnace oil had less time for its conversion to gas resulting in higher production of liquid.

Table 5.6 Nitrogen Flow rate v/s Product Yield Data for Furnace Oil Pyrolysis

Fractions	**Nitrogen Flow rate (ml/min)**		
	30	50	70
Gas	68	65	60
Oil	20	25	30
Char	11	8	5

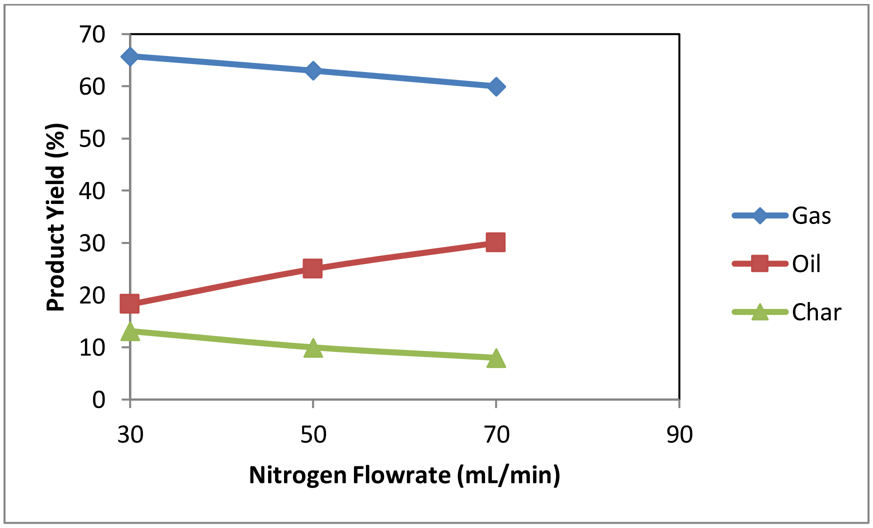


Figure 5.4Nitrogen Flow rate v/s Product Yield for Furnace Oil Pyrolysis

5.8 Effect of Temperature on Syngas Composition

The effect of temperature on synthesis gas composition during pyrolysis of furnace oil is given in table below. It can be finally concluded that hydrogen gas productivity has been changed from 34.9 to 54 mole %. Also, that of carbon monoxide has been decreased from 32 to 19 mole % by rising temperature from 650 to 800^{0}C. However, methane and ethane yields remained constant in the temperature range of 650-750^{0}C. However, it is also observed that at 800^{0}C, a sudden Temperature v/s Calorific Value for Furnace Oil Pyrolysis major decrease in yield of methane and ethane, from 22 to 12 mole % and from 7.2 to 5.8 mole % respectively was seen.

Since temperature rises from 650 to 750 ^{0}C, the production of hydrogen is increased with increase in temperature and that of all remaining other compounds has been decreased. Because, high thermal cracking takes place at high temperature so furnace oil has been decomposed to syngas and lighter hydrocarbons.

Table 5.7 Temperature v/s Syngas Composition Data for Furnace Oil Pyrolysis

Components (Mole %)	**Temperature(^{0}C)**			
	650	**700**	**750**	**800**
H_2	34.9	35.7	39.3	54
CO	32	29.5	24.6	19
CO_2	0.2	1.3	1.1	1
CH_4	24.2	23.5	22	12
C_2H_6	8	7.5	7.2	5.8

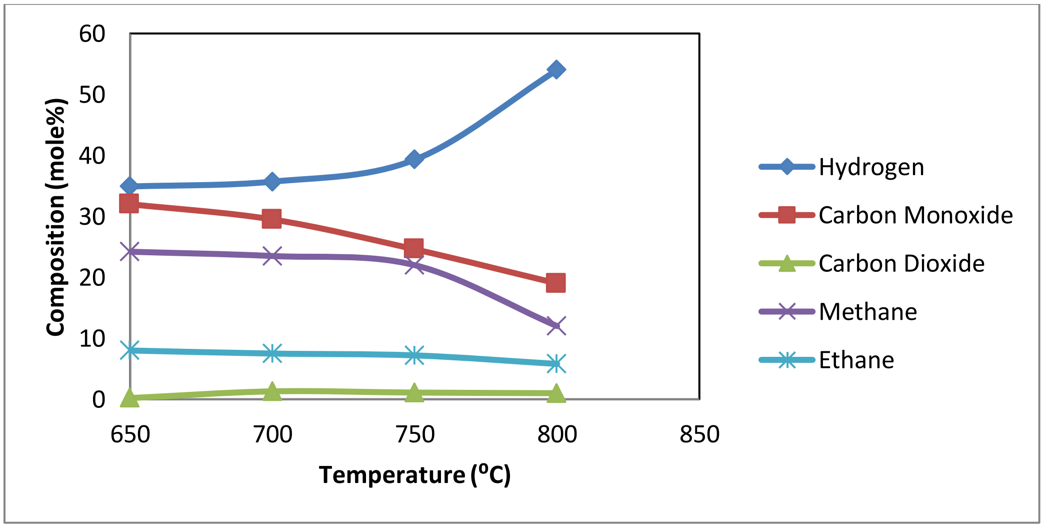


Figure 5.5Temperature v/s Syngas Composition for Furnace Oil Pyrolysis

5.9 Effect of Nitrogen Flow Rate on Syngas Composition

The influence of Nitrogen gas flow rate on product gas composition has been presented in table below. The effect was not noteworthy in the lower flow range of nitrogen. By increasing nitrogen flow rate up to higher flow of 70 mL/min, hydrogen yield has been reduced and carbon monoxide production rises along with a very small increase in hydrocarbon (methane and ethane) production. This concludes that carbon monoxide and lighter hydrocarbons are primary pyrolysis products and are important for furnace oil pyrolysis.

Table 5.8 Nitrogen Flow rate v/s Syngas Composition Data for Furnace Oil Pyrolysis

Components (Mole %)	**Nitrogen Flow Rate (ml/min)**		
	30	50	70
H_2	46	48.6	38.6
CO	14.9	16	22.2
CO_2	1	1.9	0.7
CH_4	33.3	33.3	34.6
C_2H_4	3	2.5	3.6

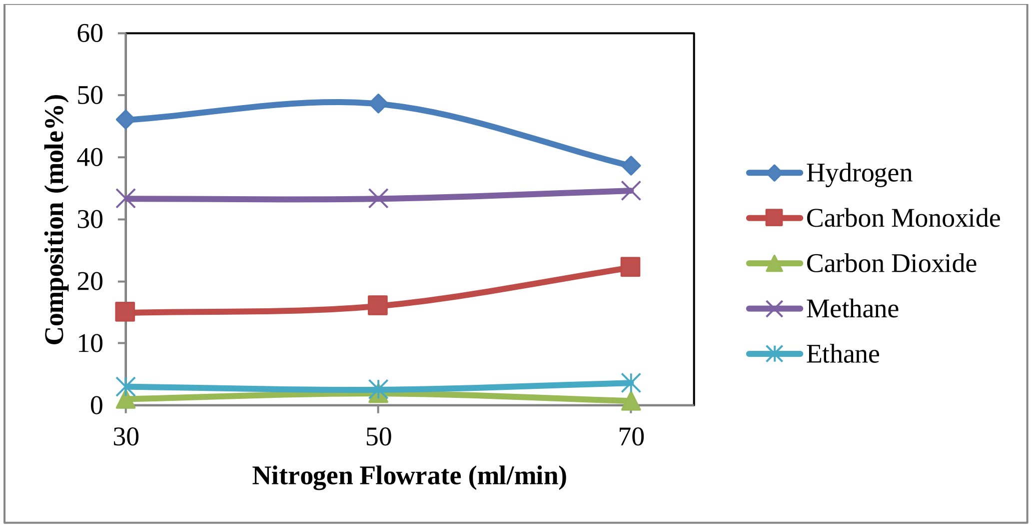


Figure 5.6 Nitrogen Flow rate v/s Syngas Composition Data for Furnace Oil Pyrolysis

5.10 Effect of Temperature on Syngas Calorific Value

The effect of temperature on product gas composition is shown in table below. The calorific value of product gas has been reduced only to some extent over the range of temperature 650-750 ^{0}C with a drastic decrease at a temperature of 800 ^{0}C, this was in fact due to the decrease in hydrocarbon production and composition also large amount of syn gas production.

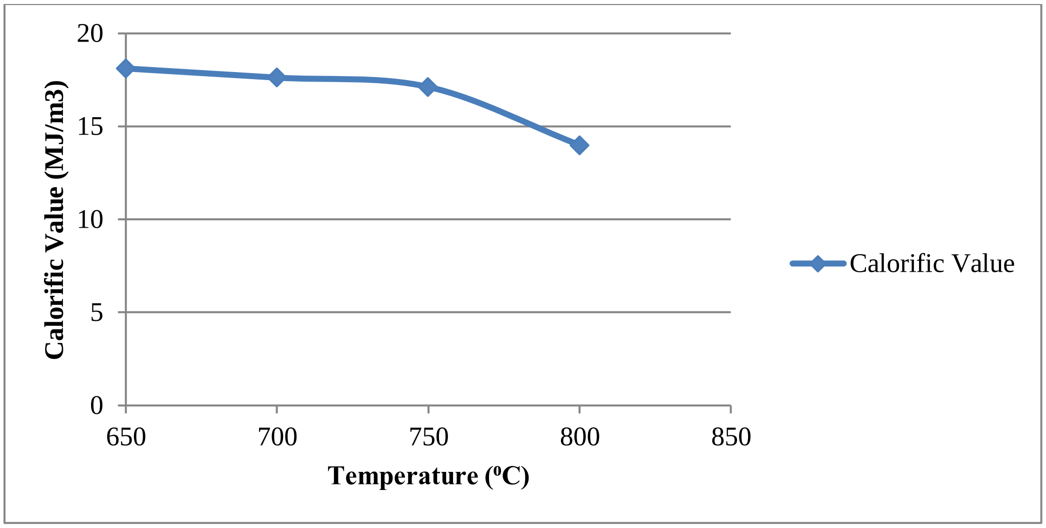


Figure 5.7Temperature v/s Calorific Value for Furnace Oil Pyrolysis

5.11 Effect of Nitrogen Flow on Syngas Calorific Value

A very small increase in calorific value was observed by increasing nitrogen flow rat. This fact was due to increase in hydrocarbons like methane and ethane production rate. Calorific value of methane is 37 MJ/m^3 which is much higher than those of hydrogen 12.76 MJ/m^3 and carbon monoxide that is 11.7 MJ/m^3. Nitrogen gas flow rates have not resulted in major effect on the production of synthesis gas. Nitrogen gas flow rate of 50 mL/min has been selected for further studies in order to obtain the high volume of synthesis gas and product gas produced and subsequently low char yield.

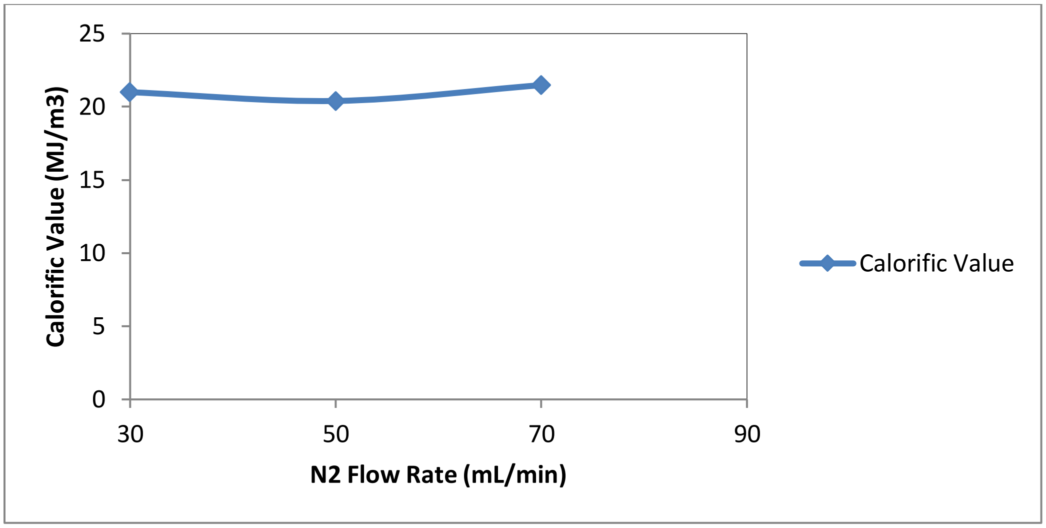


Figure 5.8Nitrogen Flow rate v/s Calorific Value for Furnace Oil Pyrolysis

CHAPTER 6

Conclusions & Recommendations

6.1 Conclusions

Limited energy resources, fossil fuels depletion and constrict emission standards has led the researcher to produce alternative renewable fuels. To reduce the gap between energy production and consumption, focus has been emphasized on finding technologies for waste to energy conversion. Pyrolysis has proved itself as an advantageous technology that converts waste material in valuable fuel grade products. Pyrolysis is an environment friendly waste treatment method because it occurs in absence of oxygen. It is a flexible process in which operating parameters such as temperature, residence time and heating rates are easily varied. Pyrolysis of heavy furnace oil resulted in the generation of fuel grade products. A number of different reactors can be used for pyrolysis depending upon feed stock and operating conditions.

Pyrolysis of furnace oil was performed in a pyrolysis chamber heated with a tubular furnace at a range of temperatures from 650-800^{0}C. Since pyrolysis was carried out in inert environment so there are negligible chances of sulfur and nitrogen oxides emissions. That makes it an ecofriendly technology. Different tests were conducted to determine pyrolysis products yields, syngas composition and calorific value.

Increasing pyrolysis temperature has been resulted in high gas yield and low liquid yield. . With increase in temperature from 600-900 ^{0}C, gas yield increases significantly from 40.89 to 65.78 %. The experiment showed that maximum liquid yield of 33.44 % was obtained at 600^{0}C. Liquid production shows a decreasing trend. Char also shows a modest increase with increasing temperature. The reason is higher degree of thermal cracking and de-volatilization at high temperature. By increasing nitrogen flow rate from 30-70 ml/min, liquid yield has been increased. Whereas, gas and char followed a decreasing trend. The residence time of furnace oil in pyrolysis chamber has been decreased due to increased carrier gas flow rate.

The effect of temperature on synthesis gas composition during pyrolysis of furnace oil has showed that hydrogen gas productivity has been changed from 34.9 to 54 mole %. Also, that of carbon monoxide has been decreased from 32 to 19 mole % by rising temperature from 650 to 800^{0}C. By increasing nitrogen flow rate up to higher flow of 70 mL/min, hydrogen yield has been reduced and carbon monoxide production rises along with a very small increase in hydrocarbon (methane and ethane) production. Syngas calorific value that is produced from furnace oil pyrolysis showed that it can be used as a fuel.

6.2 Recommendations

The following recommendations are made for further exploration of furnace oil potential in energy production.

- A study should be done to investigate how the other pyrolysis parameters such as heating rate and particle size effect pyrolysis product yield and syngas composition.

- In depth study on the calculation of activation energy required to pyrolyze furnace oil.
- Study on finding out of best pyrolysis reactor to obtain high gas yield and best fuel properties such as calorific value.
- Kinetic modeling of pyrolysis reactor to optimize pyrolysis operating parameters

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