ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

TITLE: MODELLING, SIMULATION AND EXPERIMENTAL STUDY OF CONTINUOUS WASTE TIRE PYROLYSIS PLANT

A Thesis Submitted to the School of Mechanical and Industrial Engineering in Addis Ababa Institute of Technology, In Partial Fulfillment of the Requirements for the Degree of Masters of Science in Mechanical Engineering

(Thermal Engineering Stream)

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Addis Ababa, Ethiopia

June 2019

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DECLARATION

I, the undersigned, declare that this thesis is my original work and has not been presented in any university, and that all the sources of materials used for this thesis has been duly acknowledged.

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ACKNOWLEDGEMENT

First, I would like to thank almighty God for everything he has undoubtedly done for me and the courage to finish this thesis. Secondly, I would like to express my deepest gratitude to my advisor Dr. Ing Wondwossen Bogale, for his consistent inputs and involvements in my research. I especially appreciate his patience and warm encouragements on the overall study and prototype fabrication stage. Thirdly, I would like to thank Mr. Haileleul Sahle (Phd Candidate) and Negarobe engineering staffs for their skill, time and effort on the production of such pyrolysis reactor within short period.

Finally, I would like to thank my family and friends for their priceless contributions with moral and material support throughout my academic carrier.

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Abbreviation and Acronyms

Bi	Biot number
Cp	Heat capacity (J Kg^{-1} K^{-1})
E	Activation Energy (J mol^{-1})
h	Heat transfer coefficient (W m^{-2} K^{-1})
K	Arrhenius Kinetic constant (s^{-1})
A	Pre-exponential factor (s^{-1})
Lc	Characteristic initial size/length of tire sample (m)
R	Universal gas constant (8.314 J mol^{-1} k^{-1})
T	Temperature (K)
B	heating rate (^{o}c min^{-1})
Fjo	Rate of flow into the system (mol/time)
Gj	Rate of generation (mol/time)
Fj	Rate of flow out of the ystem
X	rate of conversion
V	Volume of reactor
Hp	Enthalpy flow of feedstock
Qin	Heat inflow
Qloss	Heat loss from reactor sidewalls
TGA	Thermogravimetric analysis
DTG	Derivative thermogravimetric
NR	Natural Rubber
BR	Butadiene rubber
SBR	Styrene-butadiene rubber
HDPE	High density polyethylene
HZ	Hertz (frequency)

ABSTRACT

The present work aims at utilizing the available and untapped source of energy found in every household backyard usually termed as waste tire, using a thermal conversion method called Pyrolysis. Where the ultimate objective is, to extract the energy rooted in tires through pyrolysis process by utilizing the calorific values with an auger/screw pyrolysis reactor plant. In pyrolysis process, organic (carbon containing) compounds are heated in an oxygen free environment where tire material decomposition based on kinetic modeling expected to reveal main product lumps: Non-condensable gas, pyrolysis oil and char. This technology grants the efficient energy conversion while fulfilling the basic 3E (Environment, Efficient ad Economy) factors that leads to securing an alternative energy source. The first phase of the project is completed by waste tire characterization whilst performing the kinetic behavior under pyrolysis process and continues with the kinetic modeling and analysis of pyrolysis process with MATLAB software along with the fabrication of screw reactor where the conducted experimental approach revealed the viability of theoretical data.

Waste tires, physically treated to a particle size of 5mm were pyrolyzed in a screw reactor with a temperature range of 450-550 °C without a carrier gas. The yields pyro oil, char and gas obtained were quantified. Pyro-oil yields were 2.4 wt. %, gas 43.4 wt. % and char 54.2 wt. %. In general, the screw reactor configuration in pyrolysis of waste tire have potential to recover high valued by products in an efficient manner.

CHAPTER ONE

1. INTRODUCTION

Our planet earth is intact with an indescribable resources to human kind where most of them are likely to be declared as vital so as the human being cannot even survive without. Still with the drastic increment on world population size and corresponding diverse energy demands, our planet continues to deliver these precious resources. Unlikely, the curiously crafted human kind have been vigorously exploiting earth resources where the energy supply is to a large extent based on fossil fuels (oil, natural gas, coal), of which these reserves are finite. Given to the fact that the growing world population, increased energy demand and indication of global warming; the need for alternative means of energy sources became a sole option on preserving clean environment while meeting the energy consumption per capita.

Among the various methods of preserving clean and safe environment is the reuse of waste products into clean usable form. In relation to the evolving technological advancements, vehicle technology is regarded as a pioneer one that is widely known to human kind. Within this, the foremost mentionable component of vehicles is the ring shaped thick rubber where it is fitted onto the wheels of vehicles, buses and bicycles known as tire.

Tires are made up of numerous rubber compounds, carbon black, fillers like clay and silica, and chemicals and minerals added to allow or accelerate vulcanization. In addition, tires have several types of fabric for reinforcement and several kinds of steel. They contain so many different compounds and ingredients because they are engineering miracles, expected to handle the tortures of heat and cold, high speed, abrasive conditions, and often not enough air pressure. Tires are also expected to perform for tens of thousands of miles and retain their essential properties despite horrendous driving habits and sometimes poorly maintained or built roads [1].

Even if their positive technological impact is widely appreciated, the world is facing a massive rubber waste disposal problem. The global rubber scrap figure stands at 10-16 million tons and almost 60% of this comes from tires as reported by Eco-fiber Mouldings. The increased demand of new vehicles in developing country like Ethiopia, leads to a further significant increase of tire consumption. Used tires, rejected or unwanted ones are classified as “Waste/scrap tires” and need to be managed responsibly. Disposal of tires is now an environmental threat which led the increased interest on recovery of wastes, alternative processes for tire recycling have been considered with the goal of recovering some of the value in the scrap tires. There are several routes for upgrading waste tires, which mainly based on two strategies: Energy production by incineration or combustion or recovery of their components by hydrogentation, liquefaction or pyrolysis [2]. Among those processes, pyrolysis can be referred as a thermo-chemical decomposition of tires into a range of useful products, either in the total absence of oxidizing agents or with a limited supply, that does not permit gasification to an appreciable extent [5], where the volatile organics present in scrap tires are decomposed to gases and liquids which could be used as fuels or as a source for chemicals including benzene, toluene, xylene and limonene. The inorganic components, mainly steel and non-volatile carbon black, remain as a solid residue, which is a suitable raw material for production of carbon black or active carbon. Process conditions can be optimized to maximize the yield of char, oil or hydrocarbon gases [3]. Since rubber from tires have a calorific value higher than coal as well as considerable amount of carbon black, it seems reasonable to find a route to take advantage of its high energetic and raw material potential in order to progress in the search of alternative fuels, Co_2 emission mitigation and the reduction/recycling on raw materials. [9].

Pyrolysis is considered as one of the most feasible solutions that may be economically profitable at large scale. The interests centered on the fact that, the products obtained by this process can be easily handled, stored and transported as reported by [2]. This method not only allows for partial recovery of energy but also for utilization of the by-products (material recycling) and can be executed with an environment-friendly way. The pyrolysis products include volatile compounds, which can be partly condensed resulting in liquid (oil) and gaseous fractions. The solid remainder (approx. 30 - 40% of tire mass), mostly composed of char, can be recycled and utilized after purification for manufacture of new tires [4]. On usual basis, the process is carried out in an inert atmosphere (introducing an inert gas to purge out oxygen to prevent the secondary reactions such as thermal cracking, re-polymerization, re-condensation and char formation as stated by [9] under normal pressure and temperature typically between 300 to 650°C compared to 800 to 1000°C for gasification [5].

As discussed on the above statements, pyrolysis involves the breakdown of large complex molecules into several smaller molecules. The products are classified into Solid (mostly char or carbon), Liquid (tars, heavier hydrocarbon and water) and Gas (CO_2, H_2O, CO, C_2H_2, C_2H_6, C_6H_6, etc) which the relative product amount is greatly depends on several factors including the heating rate and the final temperature reached by the feed [5]. The key influences on the product yield (gas and oil composition), is the type of reactor used which in turn determines heating rate and the final temperature [20]. Detailed reviews regarding the pyrolysis reactors type and elemental factors that are involved in tire pyrolysis process will be briefly discussed chapter two.

This study envisages on covering the modeling and simulating a continuous waste tire screw pyrolysis plant with major findings from the kinetic modeling while validating the data with the experimental approach. For the most part, this paper focuses on the optimal design of the pyrolysis reactor with an account of heat and mass transfer. Having all the interest to yield valuable products (mainly gas and liquid from waste tires) through pyrolysis, this research finding intends to portray the potential of waste tires as a source of energy towards Ethiopian waste disposal culture.

1.1. Problem statement

Upon the review phase, the pyrolysis of waste tires have been found to be a respectful technological solution that meet the 3E's (Environmentally friendly, Economical and Energy Efficient) pillars of successful technological finding. Since, the ever-growing vehicle demand in Ethiopia is causing the production of wastes tire, where the landfills are becoming occupied with tire leftovers that remained from low efficient small scale recycling projects/methods like recycled bags, traditional slippers, rethreading etc.

The observed enduring recycling applications of waste tires do not take full advantage or potential of tires to be used a source of fuel. The majority of rubber wastes are considered as discarded tires from vehicles and reusing these wastes by environmentally respectful way can have positive impact over resource utilization and fulfilling the existing immense energy demand. Therefore, introducing an environmental safe and efficient waste tire recycling technology to the country is essential.

Furthermore, among renewable energy technologies, the waste tire pyrolysis option can be regarded as a means of alternative fuel for use of industries (use of pyro-oil as furnace oil) with socio-economic benefits.

1.2. Objectives

1.2.1. Main objectives

The main objectives of the research is to model, simulate validate the experimental study on continuous (auger reactor) pyrolysis plant to provide statements for large-scale productions as per the findings. In addition, this project foresees to contribute a reliable technological solution on preserving the environment from emissions of potentially harmful compounds to the atmosphere, soil and ground water by recycling the waste tires.

1.2.2. Specific objectives

Detailed and targeted objectives of the research

1. To understand the theory of pyrolysis and the corresponding kinetic behaviors of tires
2. To prepare and characterize waste tire (feedstock) to the pyrolysis process
3. To formulate a MATLAB code to mathematically model and analyze (simulate) pyrolysis reaction kinetics of waste tire
4. To size, model and manufacture a pilot screw type pyrolysis reactor, conduct test runs, produce pyro-oil, char and gas

1.3. Delimitation /Limitation of the paper/

The intended research study anticipates to portray the feasible and alternative source of energy from waste tires by which the study area focuses on the main reactor and manipulation of the factors that greatly influence the product yields. Since, the title declared as a continuous pyrolysis plant; the research study area will not focus on the tire crushing methods but suggests applicable crushed size ranges/particle sizes for better homogenous product yields and by product treatment.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. General overview of waste tire Pyrolysis process

Waste tires were tried to be evaluated by a number of method such as re-processing, burning and other alternative means. However, all of these methods have drawbacks and limitations on which pyrolysis process of these precious wastes was found to be the most appropriate method of recovery which produces liquid fuel, gas and char [15].

Pyrolysis is a thermo-chemical decomposition of feedstock occurring in the absence of oxygen. The word is derived from the Greek words “pyro” meaning fire and “lysis” meaning decomposition or breaking down into constituent parts [6]. As history records reveal [5-6], pyrolysis process was widely practiced in the early times (Iron Age) to produce charcoal from biomass using slow pyrolysis process (the biomass is heated slowly in the absence of oxygen at a relatively low temperature (~400°C) over an extended period of time). Technically, ’pyrolysis’ refers only to thermal degradation without oxygen; in general, (regardless of the oxygen concentration) this mechanism referred as thermolysis. In the presence of air, the carbonous residue may oxidize. The combustible gases released during the pyrolysis may also ignite, leading to combustion in the gas phase. This increases the gas temperature, with the results being slightly faster degradation than in inert ambient [13].

The term reverse polymerization, thermal polymerization or polymer cracking has been referred for pyrolysis. The main advantage of this process is that, it can deal with wastes where reusable products can be produced [9]. This thermochemical treatment can be used for feedstock recycling transforming solid wastes into high calorific fuels, chemicals, monomers or other valuable materials. Where in case of solid materials, pyrolysis releases high energy density volatile gases (condensable high molecular weight compounds and non-condensable low molecular weight products referred as pyro gas or syngas) and high energy density carbonaceous solid known as char or pyrolytic CB (Carbon black) where most of the fixed carbon and ash are trapped [9].

An in-depth knowledge of pyrolysis mechanism is very important for reactor design and product profiles. When tire particles gets heated in a pyrolysis reactor, the pyrolysis occurs when the particles surface reaches a certain defined temperature. There are two stages in pyrolysis: primary pyrolysis and secondary cracking. Vapour or volatile products are first produced from waste tires and are made up of a wide variety of hydrocarbons that can then encounter the secondary reactions [14]. Cracking occurs at higher temperatures and enables primary products to be converted into compounds, which may have a higher market value. As [14] indicates, higher market value can be achieved by a method of aromatization where maximum yields of aromatic components at a temperature between 700 ˚C & 800 ˚C. Fuel oil/pyro oil was produced without much gas at low temperature (below 500 ˚C) and the char formation was found to decrease as temperature increased from 300 to 720 ˚C.

The pyrolysis reaction scheme, as [9] reviewed it, rubbers are characterized by Carbon-Carbon double bonds and that thermal decomposition produces highly reactive radicals, which are often sub-units of the original rubber molecule. Additionally, the radical chain reaction pathway of thermal degradation process comprises hydrogen transfer steps along with the progressive breaking of the polymer backbone. Along with [9] conclusions with the stages of pyrolysis, [16] also classified the reactions involved in the tire pyrolysis into three groups: Primary pyrolysis reaction (250-520 ˚C), secondary post-cracking reaction of pyrolytic volatiles (600-800 ˚C) that strongly affect Benzenes, toluene and xylenes (BTX) yields and pyrolytic CB gasifying reaction with $CO_2/H_2O/O_2$ in the gases (750-1000 ˚C). It has been reported by the authors that, these reaction groups are dependent on the temperature and reaction time.

Since, pyrolysis follows complex routes that strictly cannot be expressed as a single chemical reaction; an empirical formula based on the mass conservation law enables a workable and feasible pyrolysis scheme [9]. In general, pyrolysis of waste tire is decomposed to form solid and volatile fractions. With this regard, several studies demonstrated that, to some degree, the decomposition of the organic part of tires can be related to the decomposition of its separate components, i.e: Extender oil, natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR)

2.2. Brief pyrolysis mechanisms and dictating factors

Pyrolysis process in general, is mainly dictated by two factors, namely 1) the physical heat transfer and 2) chemical kinetics. The process begins with the external heat source increasing the temperature of the fuel. The increased temperature results in pyrolysis reactions, forming volatiles and char. These volatiles further transfer heat to un-pyrolysed fuel, after which some of these volatiles condense to produce tar [24].

For any reaction to occur bonds have to be broken and new ones made. Breaking of bonds consumes energy and this minimum energy needed before a reaction can start is an Activation energy. In its general sense, pyrolysis consists of heating solid raw materials in an oxygen free atmosphere causing organic components to thermally decompose through complex reactions [27].

2.3. Tire compositions and feed stock elemental analysis

As Juan Daniel, 2012 [9] states, tires are made of rubber (60-65wt. %), carbon black (25-35%) and the rest consists of accelerators and fillers, which are added during the manufacturing process. The carbon black is an amorphous carbon of quasi-graphitic structure produced primarily by partial combustion of fossil hydrocarbons. It plays vital role in strengthening and providing an abrasion resistance to the rubber. The remaining percentage is due to organic and inorganic fillers (about 7 wt.% and 3wt. %) due to the addition of extender oil (a mixture of aromatic, naphthenic and paraffinic hydrocarbons) in order to soften the rubber and to improve the workability.

In reference to, Rubber manufacturers association, 2004; a descriptive composition of tires narrated in a category of passenger and truck tires

Common materials/descriptions	**Passenger tire**	**Truck tire**	**Remark**
Natural rubber	14%	27%	-
Synthetic rubber	27% (butadiene rubber)	14%	-
Steel	14%-15%	14%-15%	-
Fabric, Filers, Accelerators, Anti-ozonants etc	16%-17%	16%-17%	Polyester, nylon, aromatic oil, coumarineresin,silica, bonding agent, stearic acid, antioxidant, processing chemicals, sulfur, zinc oxide
Average weight	New: 11.3 Kgs & Scrap: 9.1 Kgs	New: 54.4 Kgs, Scrap: 45.35 kgs	

Table 2-1 Composition of tires [Rubber manufacturers association, 2004]

Regarding the intended pyrolysis process, the amount of volatile matter should correspond to the amount of gas and liquid to be obtained in the pyrolysis process whilst the amount of non-volatile matter should coincide with the solid residue remaining after pyrolysis as described on figure 2.1. Researchers have reported that, the thermal decomposition behavior of scrap tires depends on the type of rubber and contents [37].

Elemental/ultimate Analysis (wt. %)					Proximate Analysis on as received (wt. %)				CV [MJ/Kg]	Ref.
C	H	N	S	O	A	VM	FC	M		
83.2	7.7	1.5	1.44	6.16	5.00	66.1	27.5	1.4	33.40	[9]
74.2	5.8	0.3	1.5	4.7	n.r	n.r			31.8	[17]
80.46	8.14	0.82	3.68	6.9	13.21	63.41	21.86	1.62	36.34	[18]
86.00	8.4	0.5	1.9	3.2	4.9	66.0	29.1	0.4	38.3	[40]
85.88	7.72	0.4	1.48	2.22	5.05	62.16	31.54	1.31	39.35	[50]
82.466	7.639	0.282	0.923	8.69	25.91	62.02	11.24	0.82	26	This study

Table 2-2 Feedstock (Waste tire) characterization

C: Carbon, H: Hydrogen, N: Nitrogen, S: Sulfur, O: Oxygen, A: Ash, VM: Volatile matter, FC: Fixed carbon, M: Moisture

For the case of waste tire pyrolysis

$$\overset{\text{Waste tire}}{C_nH_mO_pS_bN} \rightarrow \overset{\text{Solid Fraction}}{C_aH_bS} + \overset{\text{Volatile fraction}}{C_xH_yO_zN_cS} \quad \dots (1)$$

From the characterized waste tire depicted on table 2.2, the following Molecular formula can be gathered, where it is normalized with respect to carbon

$CH_{1.112}O_{0.079}N_{0.003}S_{0.004}$ .... **100 wt. %**.................... Feed stock molecular formula

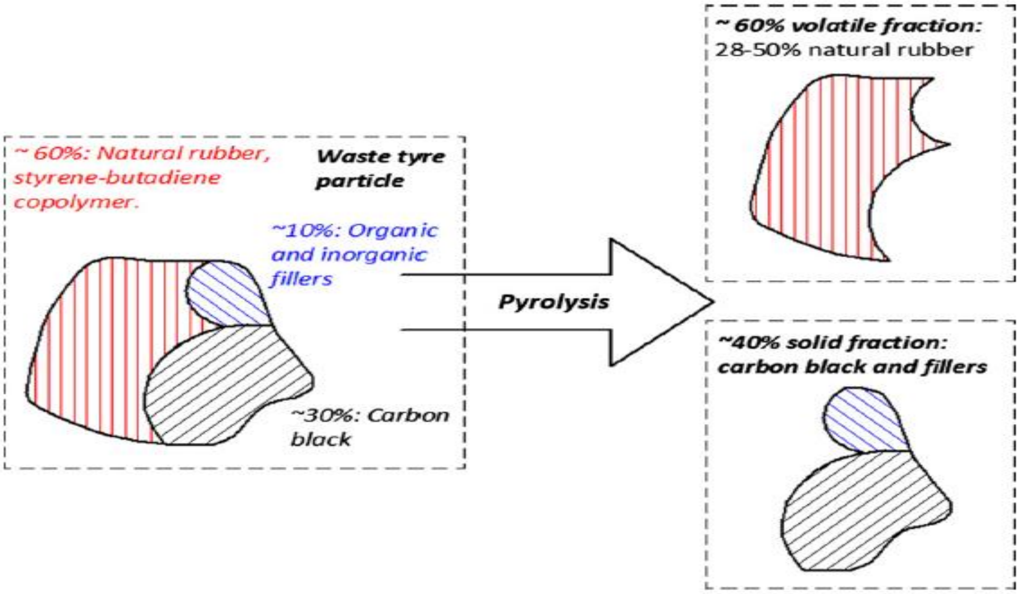


Figure 2-1 Tire pyrolysis scheme [9]

Tires are mostly composed of different rubbers, such as natural rubber (NR), butyl rubber (BR), and styrene-butadiene rubber (SBR), as well as mineral oils and carbon black (CB) [28].

Natural rubber (NR) has a vegetable origin. It is created by enzymatic processes in many plants, belonging mainly to families of Euphorbiacea, Compositea, Moracea and Apocynacea. It is industrially achieved mainly from the tree called HeveaBrasiliensis belonging to Euphorbiaceous family. From chemical point of view, Natural rubber obtained from Hevea Brasiliensis is practically pure *poly-cis-1.4 isoprene* (contains more than 99.9 % of cis 1.4 structural units) [26]

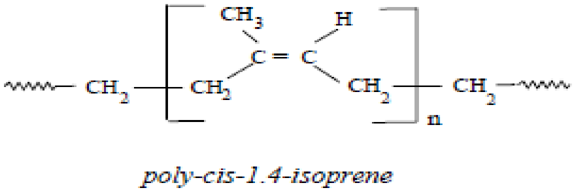

$$\sim CH_2-\left[CH_2-C(CH_3)=C(H)-CH_2\right]_n-CH_2\sim$$

Figure 2-2 poly-cis-1.4 isoprene molecular structure

Butadiene rubbers (BR) are rubbers for general use. They are produced by butadiene polymerization. It may be present in polymer macromolecules in the form of cis-1.4, trans-1.4 and 1.2 structural units. 1.2 units have pendant vinyl group, thus they may create isomeric forms (syndiotactic, isotactic or atactic). Content of individual forms of butadiene structural units in polymeric chain depends on the polymerization method and type of used initiator and it determines basic properties of BR. Presence of other structural units in poly-cis-1.4-butadiene significantly limits its crystallization ability, thus BR rubbers have low tensile strengths. Presently they are produced by means of coordination or anionic polymerization in solution [26].

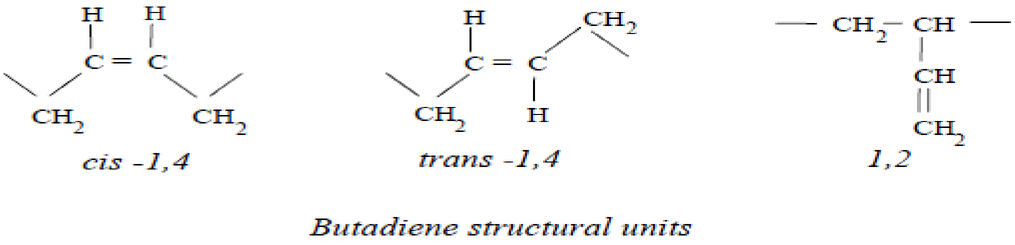


Figure 2-3 Butadiene Structural units

2.4. Process parameters that influence pyrolysis

The general pyrolysis procedure involves heating of feedstock in non-oxidizing medium at a specified rate to a maximum temperature regarded as pyrolysis/reactor temperature and holding it there for a specified time. Product natures are greatly dependent on pyrolysis/reactor temperature, heating rate, pressure, reactor configuration, feed stock, retention time of the volatile at the reaction zone, type of gaseous atmosphere [5,9,14] The initial product of pyrolysis is made of condensable gases and solid char. The condensable gas may break down further into non- condensable gases (CO, CO_2, H_2, and CH_4), liquid, and char [5]. This study will consider the effects of these process parameters on the modeling and experimental phases of study. Figure 2.4 and table 2.3 narrates influential parameter of pyrolysis process.

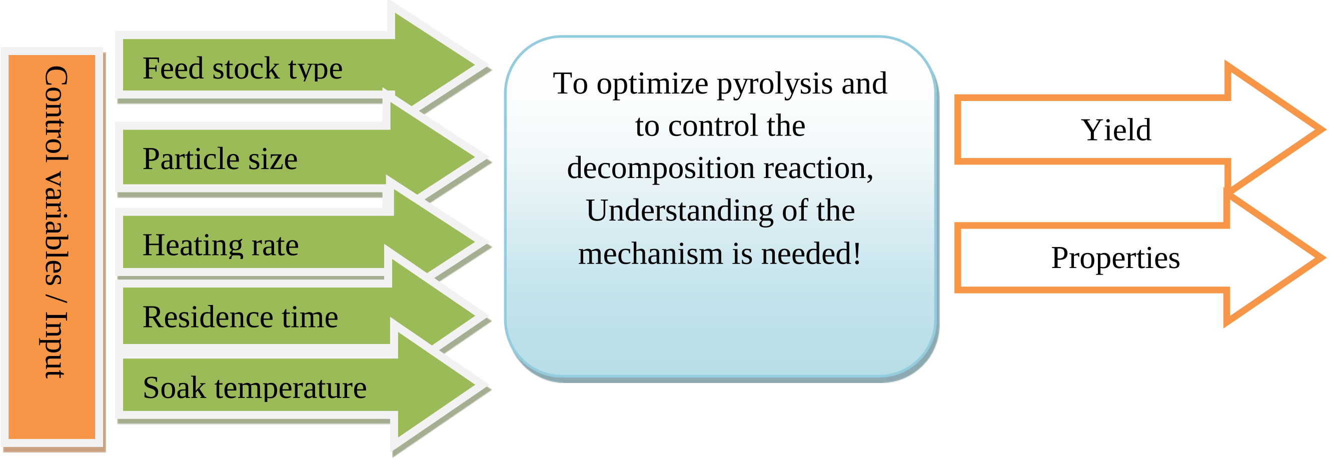


Figure 2-4 Influential parameters on pyrolysis process

Factor of influence	Effect
Chemical composition of the resin	The primary pyrolysis products relate directly to the chemical structure and composition of the resin, and also to the mechanism of its decomposition (purely thermal or catalytic)
Pyrolysis temperature and heating rate	Higher operating temperatures and high heating rates both enhance bond breaking and favor the production of small molecules
Pyrolysis time	Longer residence times favor a secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products, thus gradually obscuring the effect of original polymer structure
Reactor type	Determines mainly the quality of heat transfer, mixing, gas and liquid phase residence times, and the escape of primary products
Operating pressure	Low pressure reduces the condensation of reactive fragments forming coke
Presence of reactive gases, such as (air) oxygen or hydrogen	Such presence internally generates heat, dilutes the products and influences upon equilibrium, kinetics and mechanisms
Use of catalysts	their use influences upon kinetics and mechanisms, and hence, the product distribution
Liquid or 'gas" phase	Liquid phase pyrolysis retards the escape of evolving products, thus enhancing interactions

Table 2-3 Influential factors in pyrolysis process [47]

2.5. Basic classification of Pyrolysis and product applications

As mentioned earlier, widely known thermo-chemical conversion methods for extracting energy from an organic material are combustion (Exothermic), Gasification (Exothermic) and Pyrolysis (Endothermic). Both exothermic processes involve oxidizing process where the endothermic process consists of a thermal degradation of the initial solid fuel into gases and liquids without the oxidizing agent.

Upon the process parameters like process temperature, heating rate, solid residence time, particle size etc. the process can easily be classified into three main categories: Slow (Conventional), fast and Flash pyrolysis. Common parameters in pyrolysis process is portrayed

Pyrolysis Process	**Solid residence time (s)**	**Vapor residence time**	**Heating rate (k/s)**	**Particle size (mm)**	**Final Temp (°C)**	**Products**
Slow	450-550	5-30 min	Low	5-50	600	Char, oil, gas
Fast	0.5-10	< 2 sec	Very high	<1	~500	oil
Flash	<0.5	<1 sec	High	<0.2	≤650	oil, chemicals, gas

Table 2-4 Typical operating parameters and products for pyrolysis process [5, 6]

Slow pyrolysis: the feed is slowly heated in the absence of oxygen to a relatively low temperature over an extended time, where the vapour residence time is too high and the constituents in vapour phase continues to react with each other which results in the formation of solid char and other liquids [7]. This process has its own limitations, which make it unlikely to be suitable for good quality oil production. Due to the high residence time, cracking of primary products occurs yielding more coke, tar, as well as thermally stable products [19], which not also affect the oil yield and quality but it also consumes extra energy due to the long residence time and low heat rate.

Fast pyrolysis: the unique characteristic of this process are high heat transfer and heating rate, very short vapor/solid residence time and rapid cooling of vapors. Typically, on a weight basis, fast pyrolysis produces 60%–75% of oily products (oil and other liquids) with 15%–25% of solids (mainly char) and 10%–20% of gaseous phase depending on the feedstock used [6].

Flash Pyrolysis: the process is heated rapidly in the absence of oxygen to a relatively modest temperature range of 450 to 600 °C. The product, containing condensable and non-condensable gas, leaves the pyrolyzer within a short residence time of 30 to 1500 ms (Bridgewater, 1999). Upon cooling, the condensable vapor is then condensed into a liquid fuel known as bio-oil. Such an operation increases the liquid yield while reducing the char production. A typical yield of oil in flash pyrolysis is 70 to 75% of the total pyrolysis product [6].

The operating parameters and pyrolysis product application are diverse and to portray some (Anca-Couce, 2016)

- Pyrolytic oil: High heating rate, moderate final temperature, short gas residence time
    - Liquid fuel directly employed for heat and/or power generation in boilers and furnaces/can be upgraded to run combustion engines
    - As a source of chemical in a bio-refinery concept, biological pesticide
- Char: slow heat rate, low final temperature and long gas residence time
    - Domestic cooking fuel, for barbecuing and other energy purposes
    - Upgraded to activated carbon
- Gases: Slow heat rate, high final temperature, long gas residence time
    - Heat and power generation

Therefore, if the objective of pyrolysis was to produce the maximum amount of liquid or gas, then the rate of heating, the peak pyrolysis temperature and the duration of pyrolysis had to be chosen accordingly.

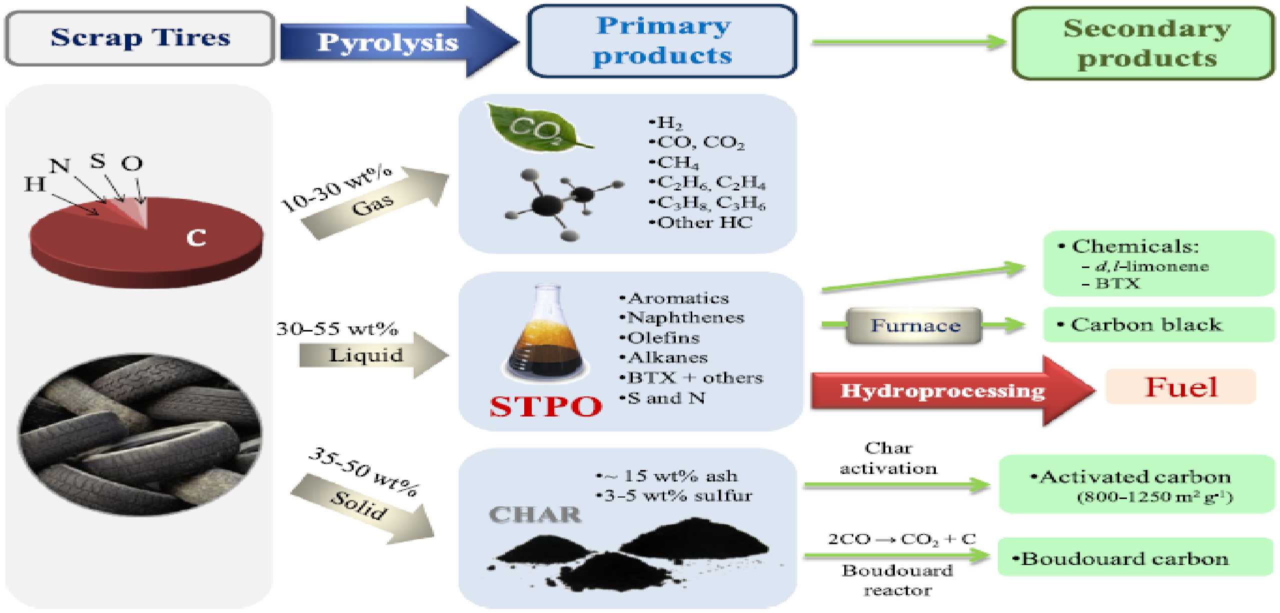


Figure 2-5 Primary and Secondary valuable product derived from Waste tire pyrolysis [12]

The liquid production in tire pyrolysis pathway with their wide range of potential opportunities for heat, chemicals, fuels and electricity applications are indicated in Figure 2-7

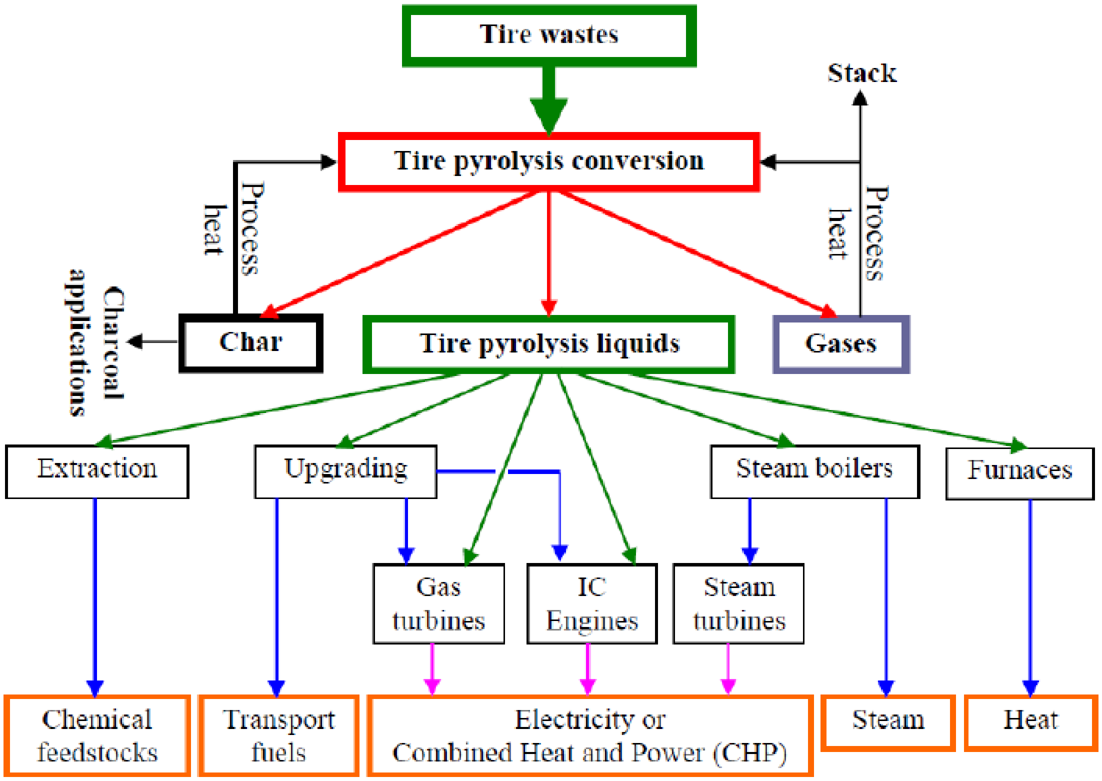


Figure 2-6 Tire pyrolysis conversion and application of products [51]

2.6. General advantages and disadvantages of waste tire pyrolysis:

Many authors [9, 14, and 15] gave conclusion on the feasibility of pyrolysis in comparison with other thermochemical processes because of its minor environmental impact and the recovery of solid and liquid material. Combustion-incineration is primarily distinguished as a destructive process and this fact makes that pyrolysis to be an efficient method for waste valorization. The major advantages can be listed as:

- It prevents air pollution and reduces carbon emission
- It is safer and more environmentally friendly than incineration, landfill and other gasification methods,
- The waste is converted into new products such as useful liquid fuel, carbon black and combustible gases

Alongside with the advantage of waste tire pyrolysis, a noteworthy problem consists of transferring the heat efficiently to drive the pyrolysis process in such a way that the temperature is evenly distributed.

2.7. Current status of pyrolysis reactor technology

In pyrolysis process, the major step is the intensification of the use of pyrolysis rectors for which a kinetic model must be appropriately maintained, in order to describe the complexity of the processes that occur during the thermal degradation of large polymer chains [30].

As a common classification, the reactor types are basically classified depending on the way the solid fuels are transported in the reactor and to list them in lump sum [31].

- Type A: No solid fuel movement through the reactor during pyrolysis (Batch reactors)
- Type B: Moving bed (Shaft furnaces)
- Type C: Movement caused by mechanical forces (E.g: rotary klin, rotating screw etc.)
- Type D: Movement caused by fluid flow (E.g.: Fluidized bed, Spouted bed, Entrained bed)

For tire pyrolysis, the panorama on reactor selection is wider on being possible to find suitable reactor, from autoclaves, rotary kilns, screw conveyors (auger), fixed, spouted, entrained and fluidized beds, rotating cone, vortex reactor, melting vessels, plasma reactors, free-fall, tubing bomb reactors, to vacuum pyrolysis. All these reactors/configurations have advantages and disadvantages in terms of technical, economical and ecological parameters were used for different energy applications such as distributed generation (heat and/or electricity) and/or the production of liquid fuels and char [9].

Depending on the aim of the pyrolysis, a specific type of reactor should be chosen by considering the unique characteristics. Figure 2-8, describes the commonly used reactor types and their schematic representations. The configurations and working principles (Inert gas & mass flow, operating parameters, product yields etc.) of different pyrolysis reactors were narrated as follows.

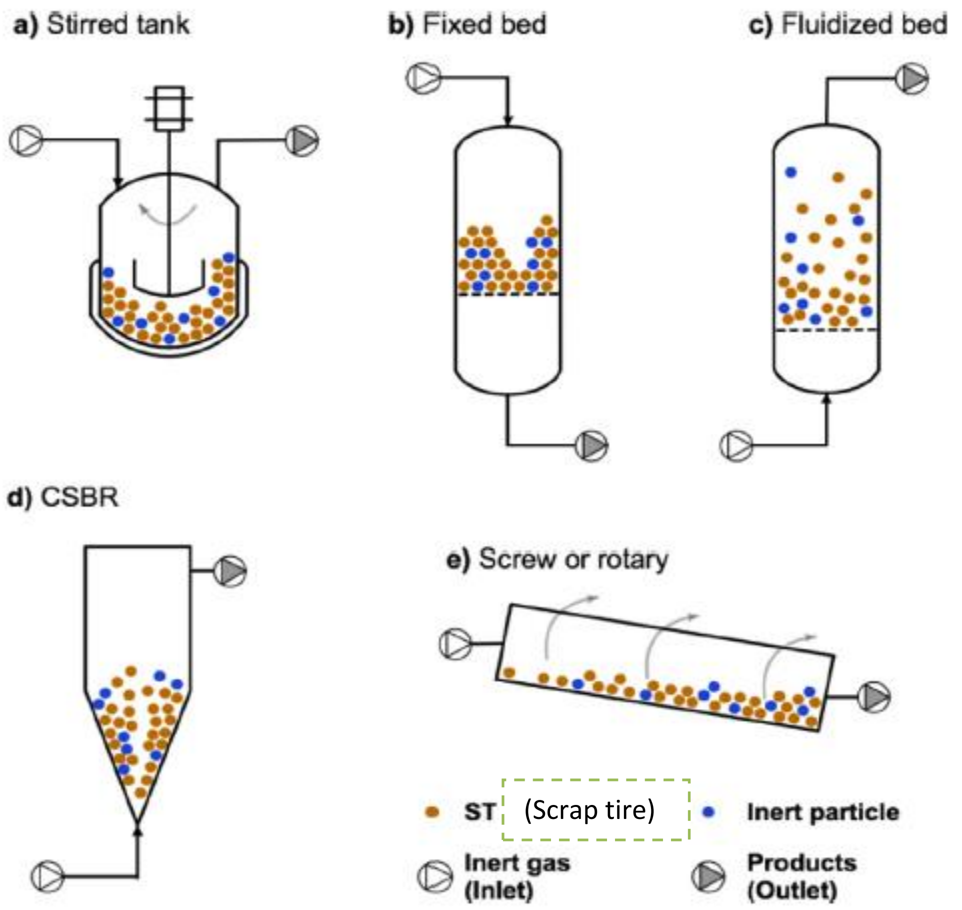


Figure 2-7 Type of reactors

2.7.1. Stirred tank

The configuration style for this reactor is based on an autoclave-type where scrap tire is fed discontinuously whereas the inert gas required for the pyrolysis and product flows continuously. With this arrangement, pyrolysis of tires under N_2 atmosphere in the 300-700 °C range for 30 min and highest yield of char at 300 °C was acquired while further increased in temperature to 700 °C, the liquid and gas yield increased to 38.5 and 17.8 wt.% [17].

2.7.2. Screw/rotary kiln

As reviewed by [17], such reactors present important advantage for large scale operation. Higher oil yields were obtained operating at 550 °C, together with the lowest gas yields. This type of reactor allows a continuous operation. The author [20] used a screw/rotary kiln reactor where it was fed by a screw feeder from the hopper containing shredded tires with throughputs from 3.5-8 kg/hr. Pyrolysis oils were condensed in a shell-and-tube condenser and non-condensable gases were combusted. The solid char was recovered at the end of the screw kiln reactor outlet. The reported maximum oil yield of 48.4 wt.% was obtained at a pyrolysis temperature of 600 °C and a tyre mass flow rate of 8 kg/h.

Diez et al. (2005) [22] also used a screw kiln reactor, externally heated by an electrical furnace to investigate the pyrolysis of shredded tire at a pyrolysis temperature of 500/600°C. The plant was designed to produce gas and very little oil, so had a long gas residence time and fast heating rate. The reported product yields were 33.5 wt.% char and 66.5 wt.% gas.

2.7.3. Conical spouted bed reactor (CSBR)

The CSBR has been proven to be a substitute for fluidized bed and an acceptable reactor for fast pyrolysis. Generally, CSBRs comprise of a central lean solid phase (spout). Solid particles enter in a fluid jet penetrating the bed from below, and a downward-moving thick solid phase (annulus) produces a counter-current flow between the solid and gas phase. At the bottom of the annular phase, solids transport downwards about the spout. It consists of three zones, which are spout region, annular space and fountain. The CSBR allows continuous operation by selectively removing the char from the bed, which avoids its accumulation in the pyrolysis reactor. In addition, the disadvantages of CSBR are the high-pressure gas requirements for spouting and attrition of the material which increase the cost of the process [34].

2.7.4. Fixed bed, batch reactor

This type of reactor is typically heated externally by an electric furnace and nitrogen or another inert gas is used as a carrier gas. The thermal degradation of tire starts at around 350°C and therefore pyrolysis experiments are usually in the range of 450-700 °C.

2.7.5. Fluidized bed reactors

The fluidized bed is heated indirectly to typical temperatures of between 500 and 780 °C via radiant heat tubes within the bed of quartz sand, in which the product pyrolysis gas is combusted to provide heat. The fluidizing gas is also the product gas and is preheated to 400 °C. Any ash build up in the fluidized bed is removed by a screw extractor. The product gases pass through a cyclone to remove particulate material and the oils condensed and distilled to produce two oil fractions, heavy and light oils. The gases undergo further removal of oil droplets in an electrostatic precipitator before storage [Williams, 2013].

Different reactor types and their product yields reported by different researchers is summarized in table 2-5.

Reactor type	**Experimental Condition**	**Maximum yield**				**Reference**
		Temp (°c)	**Oil (wt. %)**	**Char (wt. %)**	**Gas (wt. %)**	
Fixed bed, batch	400-700°C temperature	500	40.26	47.88	11.86	(Aydin and Ilkilic, 2012
Fixed Bed, Batch	500-100 °C Temp, 1200 min^{-1}heating rate	500	58.0	37.0	5.0	(Leung et al, 2002)
Fixed bed, Batch	300-720 °C Temp, 5-80 °c min^{-1} heating rate; 50g	720	58.8	26.4	14.8	(Williams et. al. 1990)
Auger reactor	N_2 flow rate, 5L min^{-1} Mass flow rate: 6.7kg/hr Reaction time: 3 min	550	42.6	40.5	16.9	(Abdulkadir, 2015)
Moving screw bed	600-800 °C temp; 3.5-8.0 Kg/hr mass flow rate	600	48.4	39.9	11.7	(Aylon et. Al, 2011)
Rotary klin	450-650 °C Temp; 12-15 Kg/hr throughput	500	45.1	41.3	13.6	(Li et al, 2004)
Fluidized Bed	450-600 °C Temp; ~200 g/hr granule tires	450	55.0	42.5	2.5	(Williams and Brindle, 2003)
Conical Spouted bed	425 and 500°C Temperature	500	~62	~35	~3	(Olazar et al, 2008)

Table 2-5 Range of Pyrolysis reactors and product yield [20]

Researchers as generally described in table 2-6, studied the pros and cons of usually practiced pyrolysis reactor types

Summary of commonly used pyrolysis reactors				
S/N	Reactor type	Advantages	Disadvantages	Authors
1	Fluidized bed	• Intense movement of particles promoted good mixing and efficient hat transfer • Scale up is easy • Suitable for fast Pyrolysis and features short residence time	• Requires small particles (2-3 mm) • Requires expensive physical treatment (grinding) • Requires a fluidizing gas	(khan,2017)
2	Screw /rotary klin	• Very good heat and mass transfer • Highly applicable for continuous operation • Simplicity of construction & operation, applicable for small scale system • Have ability to seal & resist back pressure • Lower process temperature	• Pyro-oil yield range usually lower than fluidized bed reactor • Compared to FB reactors, longer residence time is required	(khan,2017)

Table 2-6 Pros and Cons of Fluidized bed and screw type reactors

2.8. Pyrolysis mass loss and kinetics

The study of pyrolysis kinetics provides necessary information regarding the engineering design of a pyrolyzer. It also helps to explain how the different processes in pyrolyzer affect product yields and composition. The three major processes that influence the pyrolysis rate are chemical kinetics, heat transfer and mass transfer. In order to determine the role of different processes taking place in the pyrolyzer, in the final product yield and composition, non-isothermal thermo-gravimetric analysis (TGA) is employed as one of the best methods available for the study and understanding of the thermal behavior of pyrolysis [10].

As Sylvie charpenay [25] reviewed the decomposition of organic parts of tire, the decomposition of its separate components, i.e., Extender oil, Natural rubber (NR) and styrene butadiene rubber (SBR). However, there exists an appreciable uncertainty about the value of the activation energy (E) corresponding to each decomposition process.

Thermogravimetric analysis (TGA) is a standard method employed to study the decomposition reactions. The thermo-gravimetry measures the weight loss during the pyrolysis for dynamic or static (isothermal) conditions [11] and the results obtained from TGA analysis are used for the kinetic parameter estimation. At an elevated temperature, thermal degradation that occurs in the solid phases of a material, the bonds between the molecules breaks leading to release of volatile compounds and changes from the original structure of the material which regarded as a Mass loss [13].

The temperature dependent reaction rate of the pyrolysis often described by Arrhenius equation in 1889

$$K = Ae^{-\frac{E}{RT}} \tag{2}$$

and their relationship between reaction rate and temperature is given by Equation (3). Rate law as shown in equation 3 expresses the rate conversion of mass with time:

$$\frac{d\alpha}{dt} = Aexp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{3}$$

or $\frac{d\alpha}{dt} = K(T)f(\alpha)$

Where A is the pre- exponential factor (frequency factor), E: Activation Energy, R: The universal gas constant and T: Absolute temperature where α is the conversion of waste material as defined on equation (4)

$$\alpha = \frac{mo-m}{mo-mchar} \tag{4}$$

Where m_o is initial mass of sample, m and m_{char} are the actual sample mass and char yield (including ash) respectively. Assuming that the heating rate is defined as ***β=dT/dt***, equation (3) can be written as

$$\frac{d\alpha}{dt} = \frac{A}{B}f(\alpha)e^{-\frac{E}{RT}} \tag{5}$$

Estimation of kinetic parameters, such as the pre-exponential factor (A) and the activation energy (E), which are based on the kinetic theory and TGA (Thermogravimetric analysis) or DTG (Derivative thermogravimetric analysis) where kinetics of mass loss is measured by the induced evaporation of pyrolysis products and the gathered data can be made by different techniques. These techniques are known as model fitting (which could include identification of the kinetic reaction model) or model-free (i.e. iso-conversional). In the model-fitting approach, kinetic parameters are determined by assuming the form of $f(\alpha) = 1 - \alpha$ [23]

As most authors have observed, the thermal degradation of elastomers and rubbers, under nitrogen atmosphere is exothermic with a temperature centered near to 380 °C on which the exo-thrmocity proceeds likely from cycle formation and cross linking and the whole reaction can be classed as a first order reaction [38].

Recalling Eq (2), the reaction rate typically increases exponentially with increasing temperature in a fashion first parameterized by Arrhenius. The reason for temperature dependence is due to the distribution of energies at any given temperature commonly Boltzmann distribution. For uni-molecular decomposition, the Boltzmann distribution describes the probability that a given bond will be in an energetic-enough state to dissociate. Some reactions have no reaction barrier notably free-radical recombination reactions, which are important in hydrocarbon cracking [39].

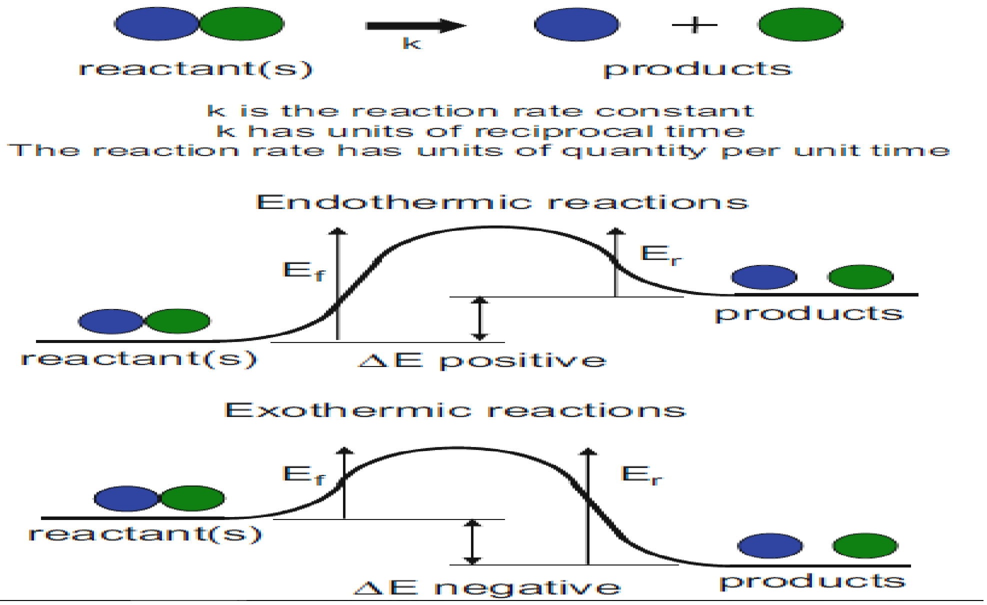


Figure 2-8 Schematic representation of chemical reaction barrier and type of reaction determination [39]

In order to overcome the activation barriers, two practical approaches are recommended by researchers

- By providing the necessary energy to form the transition state, i.e. raise the energy of the reactants by raising the temperature of the system

- Or make the activation barrier smaller, this can be done by adding a catalyst to the system which has the effect on activation energy

On experimental approach, most kinetic studies carried out in thermogravimetric equipment's, which allows the evolution of the polymer to be monitored throughout its degradation under isothermal/non-isothermal conditions. In addition, the process involved in pyrolysis of waste tires was studied by many researchers to understand the kinetics and reaction mechanisms [9-11, 30]. A popular approach to reach a better understanding is to develop appropriate mathematical models and reaction patterns. [30]

As mentioned above, works on the modeling of pyrolysis can be classified according to the type of reaction scheme chosen. Some authors contemplate pyrolysis according to a one-step reaction mechanism, while others propose several steps with consecutive reactions. The latter type, multi-reaction of modeling is found to be a reliable approach for better matching with the experimental results. [30]

As previously, discussed, different tires have different proportions of SBR, NR and BR and therefore return different Ea values. Below here, kinetic values for the pyrolysis of granulated scrap tires gathered from different authors as shown in table 2.7.

Material	Activation Energy, Ea(KJ/mol)	Pre-exponential factor, A (min-^{1})	Reference
Granulated Scrap tire (< Ø12mm)	160	2.49E10	[40]
Scrap tire	80-95.3	-	[53]
SBR NR R	152 207 215	4.5E10 2.36E16 6.32E14	[54]
Scrap tire	96-105	1.52E6-6.84E6	[55]

Table 2-7 Kinetic values of tire pyrolysis

The mean Ea and A values obtained by researchers were comparable figures which can ease the assumption on taking the mean values for further analysis.

2.9. Chemical breakdown of rubber-tire materials during pyrolysis

As H Eidesen (2018) and his colleagues described the chemical pyrolysis of HDPE, this paper also modifies the physical breaking down phenomena of tires in correlation to HDPE pyrolysis as follows (As an assumption, the portrayed process applies for tire break down phenomena);

The first thing that happens during pyrolysis is that the covalent bonds holding the Natural (NR) & Butadiene rubbers together start to break. This only takes place when tire is heated or energized beyond the reaction activation energy. The result of this breaking is that the molecules have an unpaired electron, henceforth turning into free radicals. These radicals are the key to pyrolysis. They are attracted towards the larger chains and split them into smaller chains. The chain splitting is complex and may happen in different ways, however, we can simplify to three main free radical splitting processes.

Generally, the kinetics of the pyrolysis reaction is characterized by several parallel and serial reactions (in solid and gaseous phases) involving several chemical mechanisms such as bond rupture, dehydrogenation, cyclization etc [30].

2.10. Heat transfer in a reactor and tire particles

On preceding section, the direct influence of heating rate on pyrolysis yield was discussed and it assumed that the heating rate is too high that to offer any resistance to the overall rate of pyrolysis, but this holds true for the temperature ranges of 300 to 400 °C [5]. Therefore, on higher temperatures heat and mass transport influences the overall rate and can not be neglected.

Radiation and convection type of heat transfer modes takes places during pyrolysis on particles outer surface. Within the interior of the particles, the heat transfer mode will shift to conduction and convection.

In order to ascertain isothermal temperature gradient among the tire particles, the term Biot number [dimensionless] can be used

$$Bi = \frac{hl}{K} \tag{6}$$

Where h is the film coefficient associated with convection heat transfer through the thermal boundary, L is some characteristics scale length of solid and K is the thermal conductivity of the solid. The Biot number is a positive quantity, which lies in the range: $0 < Bi < \infty$.

When the biot number is sufficiently small, eg Bi<0.2, the temperature drop through the solid is small relative to the temperature drop across the film. In this case the solid can be assumed to be nearly **isothermal**.

2.10.1. Energy requirement of pyrolysis

Martinez (2013) summarizes, the energy requirement of pyrolysis process, sometimes termed as enthalpy or heat for pyrolysis, is defined as the energy required to raise the feedstock from room temperature to the reaction one (sensible energy) and also the energy to convert the original feedstock into the pyrolysis products (reaction enthalpy). The heat demand, in the strict pyrolysis process, can be supplied by different heat sources: (i) by burning an auxiliary fuel, (ii) by burning the gas and/or solid fraction obtained in the process, (iii) by electric heating and (iv) by using hot sand, solvents or molten salts as a heat transfer medium (heat carriers).

2.11. Waste tire pyrolysis oil characterization and handling (Desulfurization, condensation)

The waste tire product (pyrolysis oil) is a brownish liquid resembling crude oil where the calorific value can be as high as 44 MJ/kg comparable to the valued fuels. It requires a separate section to be analyzed in terms of its composition and potential for being used as alternative fuel [12].

On the production of syngas (i.e.: Combustible gas) and by products of tars and chars, a range of pollutants are incorporated within the syngas created from the process (quality of process), which can hinder the plant from minimal emissions and damages the equipment. For this reason, prior to the syngas reaching to the downstream equipment, cleaning is essential.

The cleanup technologies are wet & dry scrubbing technologies, cyclones and electro-static precipitators. In reference to the below table [12], the end product properties of pyrolytic oil has reported to feature the physical properties of density and viscosity slightly higher than commercial diesel at 20˚C.

Physical properties	**Pyrolytic oil**	**Gas oil**	**Light Fuel oil**
Density (kg/L)	0.910	0.780	0.890
Viscosity 40 °C (cst)	6.3	3.3	21.0
Flash point (°C)	20	75	79
Moisture, Vol%	4.6	0.05	0.1
GCV MJ/Kg	42	46	44.8

Table 2-8 Comparison between pyrolytic oil and Fossil fuel [12]

The figures in table 2.8 could change as per the refining stages and methods of refinement. Pyrolytic oil requires preliminary treatments such as decanting, centrifugation, filtration, desulphurization and hydro treating before to be used as fuels directly (industrial furnace, power plant, boiler.) or by blending with fossil diesel.

Condensation is an important step in the production of pyrolysis oil. Without this step, only the char and gas products can be obtained from the process. The vapors generated during the process pass through the condensation unit to improve the heat transfer rate and change the physical state of matter from the gas phase into liquid phase. The major condensing fluids such as water, air, liquid nitrogen, refrigerants (hydro chlorofluorocarbons (HCFCs), Feron-12, R-410A, R-407C and R-134a), ice, chemicals (dry-ice/acetone) and ammonia (NH_3) or R-717 are commonly used [30].

2.12. Current status and challenges

As pyrolysis is a more environmentally respectful option for waste tire recycling and potential waste energy recovery system, the said potential fuel (waste tire oil) presents a series of compositional limitations for its direct implementation in an internal combustion engine, as stated on (Idoia, 2015)

I. It's high sulfur content and hetro-atomic molecules
II. High concentration of aromatics, and
III. High proportion of heavy molecules within the gasoil boiling point range (>350°C)

From an environmental perspective, these waste tire oil features are unacceptable and arouse the necessity for its upgrading for heteroatom and heavy molecule removal.

2.13. Waste tire management (Material recycling and energy recovery)

Since tires are designed to withstand harsh mechanical and weather conditions as ozone, light and bacteria, their recycling is not so much easy as the fact that they are thermoset polymers which cannot be melted and separated into their chemical components with normal environmental degradation. Tires life time in landfills is considered to be between 80 and 100 years [9].

As many authors agree and Mr. Marek et al [40] stated, tire pyrolysis will improve the economical revenue and able to solve the problem on its own. Numerous concepts and processes have been introduced so far for material recycling and some of them were successful to some extent.

In regard to material recycling/reusing, the alternative applications as in low value products were used in agriculture, landscaping, shore protection, harbors and dock, shoemaking and road construction but it is obvious that these useful application for scrap tires can only offer a limited outlet for the millions of old tires generated every year in a country [25].

Retreading of used tires on the other hand is the most preferable way of making use of old tires. On average only 15% of crude oil is needed to produce a retread instead of a new tire. Thus, the price of a tire is reduced up to 45% without any loss in quality. But, tire for passenger cars normally are retreaded once, tires for Lorries are retreaded twice and aero plane tires even up to seven times [25].

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Methodology

This research uses three approaches, namely Modelling, simulation and experimental methods. Making the technical specifications as a springboard, the conceptual design & modelling was demonstrated using a CAD tool called CATIA V5. In further, prototype fabrication (pilot pyrolyzer) for the test run is ready for use to validate the kinetic modeling done with MATLAB 2015 versus the actual results.

Final results from the test run will be analyzed to compare the feasibility of produced by products for diverse applications and to draw conclusions from the work.

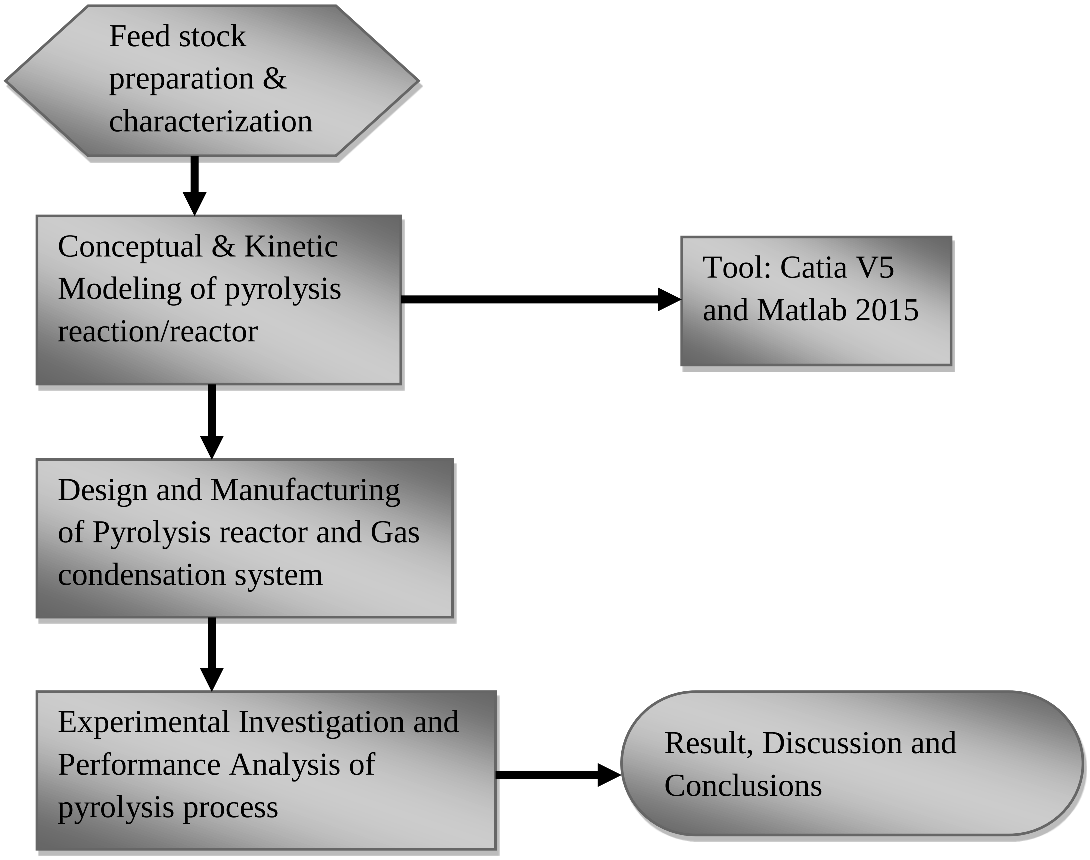


Figure 3-1 Brief Description of the methodologies used

3.2.1. Materials

3.2.1.1. Waste tire sample preparation and characterization

Use of waste tire for pyrolysis process most often requires a reduction of particle size and the widely used method is a grinding process.

In general, three current methods of grinding waste rubber are: (1) Ambient grinding, (2) Cryogenic grinding and (3) wet-ambient grinding [32]. In this paper, an ambient mechanical size reduction is adopted because all size reductions steps take place at or near ambient temperature by chopping and grinding using mechanical grinding technique to a size of near to 5mm particle size to suit for isothermal state as per Biot number.

In referring to the tire composition in chapter 2.3, tires are made up of rubbers, fillers, fabrics and steel as a major constitute. Therefore, their construction layout is according to the endurance limit and strength requirement set by tire manufacturers. For this study, the sidewall part of a light vehicle tire is used, where the initial curding is done by manual grinding.

Figure 3-1 Sample tire particles ground to a size of 5 mm

Waste tire characterization

The elemental composition of the scrap tire sample were 82.4 wt.% Carbon, 7.639 wt.% Hydrogen, 0.282 wt.% Nitrogen, 0.923 wt.% sulfur and 8.69 wt.% oxygen. The average values are taken and the characterization of tire is shown, in the following table 3-1.

Proximate analysis				
Moisture content (wt. %)	0.82			
Ash content (wt. %)	25.91			
Volatile content (wt. %)	62.02			
Fixed carbon (wt. %)	11.24			
Ultimate analysis (wt. %)			mol/100g	mol/mol C
Carbon (wt. %)	82.466	÷12 =	6.87	1
Hydrogen (wt. %)	7.639	÷1 =	7.64	1.112
Nitrogen (wt. %)	0.282	÷14 =	0.02	0.003
Oxygen (wt. %)	8.69	÷16 =	0.54	0.079
Sulphur (wt. %)	0.923	÷32 =	0.03	0.004
Molecular formula (Normalized with respect to carbon).	$\mathbf{CH_{1.112}O_{0.079}N_{0.003}S_{0.004}}$			
Lower heating value (MJ/Kg)	26 MJ/Kg			

Table 3-1 Proximate and Ultimate analysis

In addition, a pilot continuous screw reactor was constructed with an overall dimension of 2m screw conveyor with 190 mm diameter with full pitch with a design capacity to process 15 Kg/hr of waste tire.

The pyrolysis plant consisted mainly of screw reactor and gas condensation system. The screw reactor, which was indirectly hated by a biomass furnace, was made of AISI 1008 carbon steel with a length of 2 meters by 190 mm inner diameter.

CHAPTER FOUR

4. THEORIES OF PYROLYSIS, KINETIC MODELING AND REACTOR SIZING

Recalling that Pyrolysis is a thermo-chemical decomposition of feedstock occurring in the absence of oxygen, it offers an environmentally and economically attractive method of waste tires transformation into useful products and energy. It also represents one of the most important steps during the waste tire gasification. Thermo-gravimetry analysis reveals that the pyrolysis of tire rubber at atmospheric pressure starts at a temperature around 250°C and finishes at a temperature of about 550°C.

Generally, more than one degradation temperature region during rubber pyrolysis is recorded and by pyrolyzing waste tire, three fractions are obtained: solid residue (around 40 wt. %), liquid fraction (around 50 wt. %) and gas fraction (around 10 wt. %). As a common trend, an increase in yields of liquid and gas fractions is associated with an increase in temperature. From the works devoted to tire pyrolysis, which are focused on the generation of liquid fuel results that derived liquids are complex mixture of organic compounds containing many aromatics. These liquids can be separated into light and higher fractions. Thus, the derived oils may be used directly as fuels, petroleum refinery feedstock. The main components of pyrolysis gases reported by various authors are: H_2, H_2S, CO, CO_2, CH_4, C_2H_4, C_3H_6 and other light hydrocarbons [33].

4.1. Pyrolysis-The conversion alternative: Why pyrolysis?

Pyrolysis is considered as one of the most feasible solutions that may be economically profitable at large scale. The interest is centered on the fact that the products obtained by this process can be easily handled, stored and transported as reported by [2]. This method not only allows for partial recovery of energy but also for utilization of the by-products (material recycling) and can be carried out in the environment-friendly way. The pyrolysis products include volatile compounds, which can be partly condensed resulting in liquid (oil) and gaseous fractions. The solid remainder (approx. 30 - 40% of tire mass), mostly composed of char, can be recycled and utilized after purification for manufacture of new tires [4].

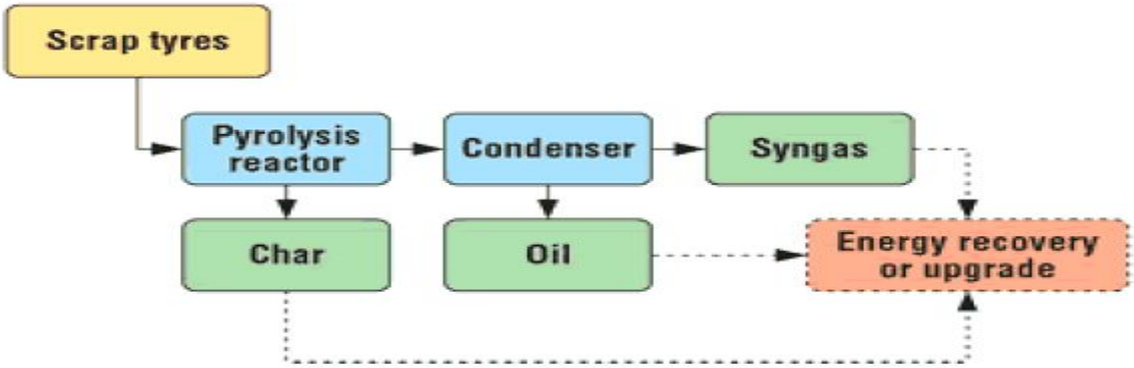


Figure 4-1 Pyrolysis process [56]

4.2. Process Zones

From a thermal standpoint, pyrolysis process can be divided in four stages. An overlap may exists on temperature dependent classifications [5]

- **Drying(<200 °C)**: Free moisture and some loosely water is released
- **Initial stage (100°C -300°C)**: Exothermic dehydration of tire takes place with release of water and low-molecular-weight gases like CO and CO_2
- **Intermediate stage (> 200°C):**it's a Primary pyrolysis taking place in temperature zone 200-600 °C where large molecules of biomass particles decompose into char (primary char), condensable gases (Vapors and precursor s of the liquid yield)
- **Final stage (~300-900 °C)**: Involves secondary cracking of volatiles into char and non-condensable gases. If they reside in the tire long enough, relatively large-molecular-weight condensable gases can crack, yielding additional char (called secondary char) and gases.

In terms of process stages, it can be characterized as the following process diagram

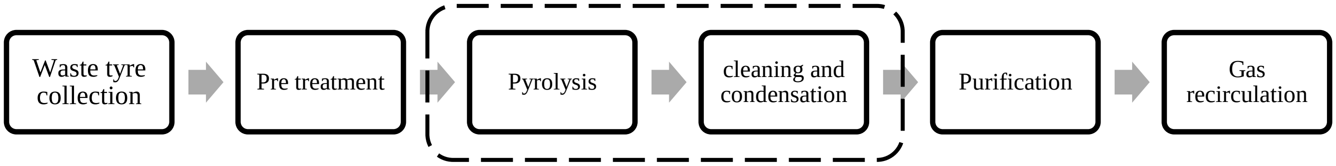


Figure 4-2 Major milestones in pyrolysis process

4.3. Pyrolysis reactor sizing and conversion with basic assumptions

4.3.1. Selection of pyrolysis system

The selection for a reactor for a specific pyrolysis application requires a consideration of several factors like: a) feed stock character and application of final product, b) desired heat transfer characteristics and c) Possibility of industrial scale up.

Getting into the selection process for suitable reactor, the physical phenomena or situations must be clearly defined so that an appropriate reactor type can be selected. Existing situations/requirements: A) Feed stock grinding is problematic, B) Small scale with simple design and operation, C) A continuous operation is required, D) Scale up to industry level with minimum capital investment

Reactor type	Thermal Efficiency (Heat transfer rate)	Design simplicity and operation	Continuous operation	Scale up to industry level	Physical treatment (Grinding, requirement of fine particles)	Requirement of carrier gas	By-Product removal system
Fludized bed	Good	Poor	V. Good	V. Good	Very High	High	V. Good
Auger/screw reactor	V. Good	V. Good	V. Good	V. Good	Moderate	Moderate	V. Good
Batch reactor	Good	V. Good	Poor	Poor	Moderate	Low	Poor

Table 4-1 Reactor selection criteria

Therefore, taking the above points as an input, Screw reactor configuration is found to be a best fit for small scale continuous operation of waste tire pyrolysis and this justification has outlined with the accompany of literatures discussed in the literature review part (chapter two).

The present study focuses on, conducting waste tire pyrolysis with an auger/screw reactor, which it comprises four main parts: The feeding system, the reactor, the vessel for solids collection and the condensing system. Both the feeding system and the reactor consist of worm screws. The reactor is heated by externally biomass-heated furnace. During reaction, waste tires move through the reactor while decomposing into a solid residue and volatiles. Whilst the volatile fraction reaches two consecutive heat exchangers by natural convection with the help of the carrier gas, the solid residue leaves the reactor falling down by gravity into a vessel for solids collection. In both condensers, the condensed fraction is recovered in a liquid collector after moving down by gravity. Finally, the non-condensed gas fraction at ambient temperature is conducted to a burner before reaching the atmosphere.

Prior to focusing the study to the reactor sizing and reaction rates, it is necessary to account for the various chemical species entering and leaving a reaction system. This accounting process is achieved through overall mole balances on individual species in the reacting system.

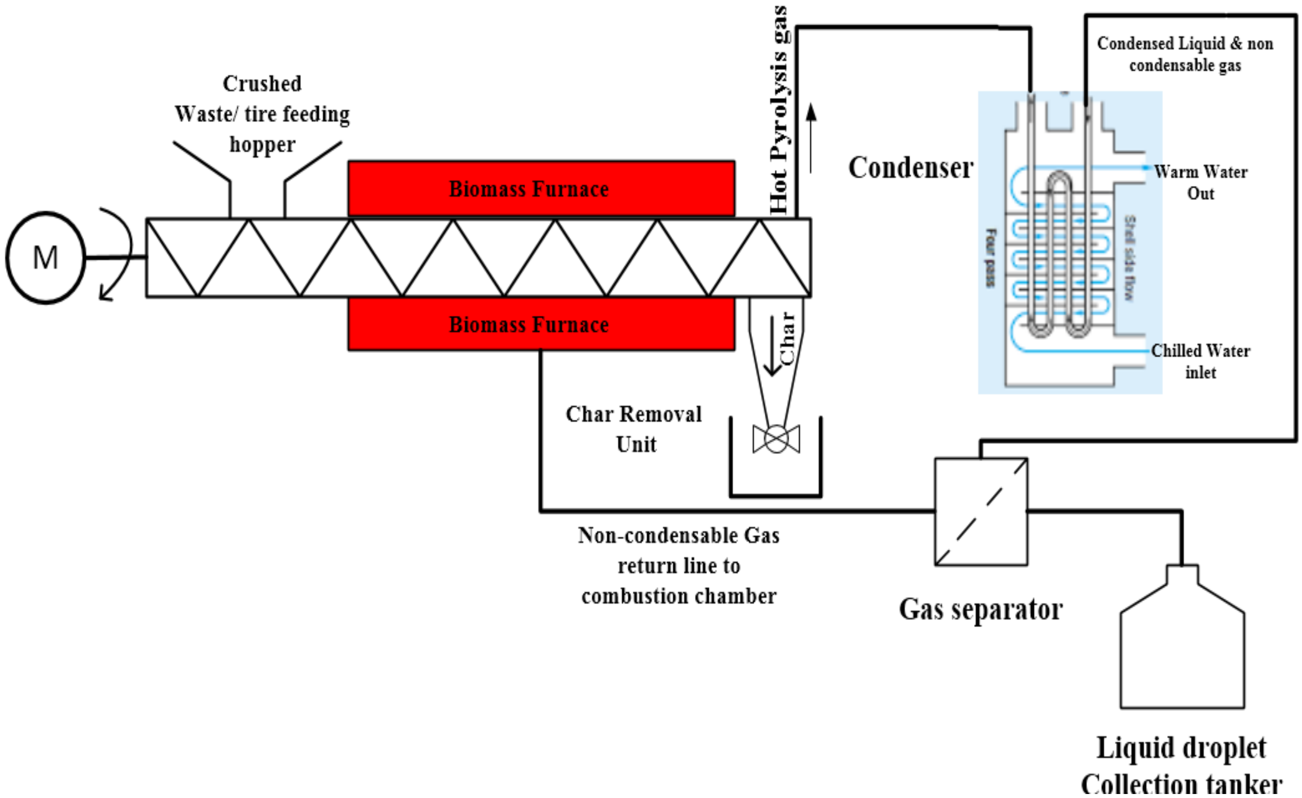


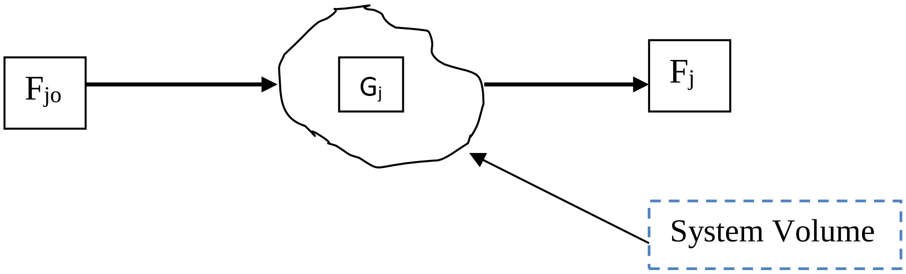
Figure 4-3 proposed layout for the tire pyrolysis plant with capacity of 15 kg/hr (original concept by [57])

4.3.2. Terms definition, preliminary design equations & mole balances

In order to justify chemical reaction has taken place, a detectable number of molecules of one or more species have to lose their identity and assume a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms. A chemical change, in its classical approach is assumed that the total mass is neither created nor destroyed when a chemical reaction occur. [35]

The rate of disappearance of a species, say species A, is the number of A molecules that lose their chemical identity per unit time per unit volume through the breaking and subsequent reforming of chemical bonds during the course of the reaction. Foggler (2004) summarizes three basic ways, i.e.: By Decomposition, Combination and isomerization. For this study, pyrolysis process as a decomposition with breakdown of molecules with the use of heat will be analyzed.

The general mole balance equation /mole balance on any system at any instant time and system boundary can be generalized by the following equation



Mole balance on species j at any instant in time, t

Rate of flow of j into the system (moles/time)	+	Rate of generation of j by chemical reaction within the system (moles/time)	Rate of flow of j out of the system (moles/time)	Rate of accumulation of j within the system (moles/time

In + Generation - Out = Accumulation

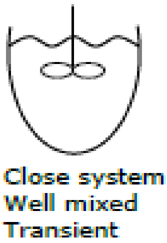
$$Fjo + Gj - Fj = \frac{dNj}{dt} \quad (7)$$

Where: F_{jo}: Is the input molar flow rate, F_j: Is the output molar flow rate, G_j: is the generation, and $\frac{dNj}{dt}$ is the accumulation (All units are moles//time)

Assumption:

- The system variables are uniform throughout the system volume, then
  $Gj = -rjV$, if reactants are consumed
  Where r_j: rate of formation of species j per unit volume and V: System volume
- If r_j changes with position in the system, Eq (7) can be written as
  $$Fjo + \int rjV - Fj = \frac{dNj}{dt} \qquad (8)$$

From this general mole balance equation, a preliminary form of the design equations of the most Common industrial reactors: batch, continuous-stirred tank (CSTR), and tubular.

Common Reactor with descriptions	**Behaviors and Assumption**	**Remark (Adjustments made on Eq 7)**
Batch Reactors 	• Neither inflow nor outflow of reactants ($Fjo = Fj$) • If the reaction mixture is perfectly mixed, r_j is independent of position	$\int rjV = \frac{dNj}{dt}$ $rjV = \frac{dNj}{dt}$ Differential equations!
Continuously stirred tank reactors (CSTR)	• CSTRs are operated at steady state (accumulation = 0) and are assumed to be perfectly mixed. This makes the temperature, concentration, and reaction rate independent of position in the reactor	• Steady state ($\frac{dNj}{dt} = 0$) • Well mixed and no spatial variation in the rate of reaction $\int rjV = rjV$ • $Fjo + rjV - Fj = 0$ • $V = \frac{Fjo-Fj}{-rj}$ (8)

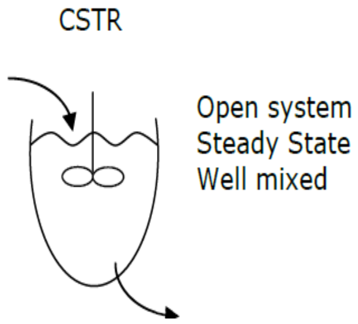
Common Reactor with descriptions	**Behaviors and Assumption**	**Remark (Adjustments made on Eq 7)**
	- For irreversible reactions, the maximum value for conversion , X, is that for complete conversion, I.e. X=1.0	- $X = \frac{Fjo - Fj}{Fjo}$ - $V = \frac{FjoX}{-rj}$ (9) $Analytical\ Equation$!!

Table 4-2 Mole balance equation for CSTR

4.3.3. Reaction kinetics and Reactor Sizing

Due to the operational similarity of continuously stirred tank reactors (CSTR) with pyrolysis reactors, the design equations for reactor sizing were adopted with a justification.

The CSTR normally runs at steady state and usually operated to be well mixed. Because of the latter quality, the CSTR generally modeled as having no spatial variations in concentration, temperature, or reaction rate throughout the vessel. Since the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus, the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. [35]

To recall the basic assumptions, that used for simplification of CSTR sizing

- Continuous process: uninterrupted sequence of operation, in which the feed material must be introduced in a schematic manner in order to maintain equilibrium condition.
- Steady state: Variables occurring within the system are constant, in spite of the ongoing processes that strive to change them. Accumulation can be ignored.

4.3.4. Kinetic modeling with MATLAB and Determination of reactor volume

As described in the literature review, the pyrolysis reaction consists of multiple steps before all tires (feedstock) are converted to the products of Carbon black, oil and gas. In addition, before the pyrolysis process reaches a steady state, Tire is also converted into an intermediate lump.

The pyrolysis reaction is a combination of multiple reactions with varying reaction constants. The reaction constants determine the rate of each reaction and may depend on the concentration of reactants and products. Temperature and presence of catalyst may also affect its value. [36]

Tire conversion, X, has been defined as the weight loss by mass unit of the initial amount tire and by recalling Eq (4) the conversion can be calculated.

The product yield of pyrolysis can be predicted by including reaction kinetics (rate of change in physical or chemical system) in the model. The modeling of tire pyrolysis kinetics gives an overview of the mechanisms that are responsible of the decomposition process and predicts the potential difficulties in the pyrolysis reactor. On this basis, the pyrolysis reaction must be presented in the form of multiple reactions in order to better understand the degradation mechanism. [30]

Besmakhiari 2017 [30], reviewed that the multi-reactions scheme of tires built upon 4 reactions in series and in parallel

1) A → V1+R1 Main split of chain
    2a. R1→ V2 Primary reactions (1&2)
    2b. R1→ R2 De-polymerization
    2c. R2→ V3
3) R2 → R3 : Cyclization reactions
4) R3 → V4+R4 : Degradation of cyclization products: Secondary reactions

Where A: Butadiene monomer or Styrene butadiene rubber
R1: Formation of first intermediate
V1, V2, V3 & V4: corresponding Volatile matters
R2 & R3: Formation of second and third intermediate

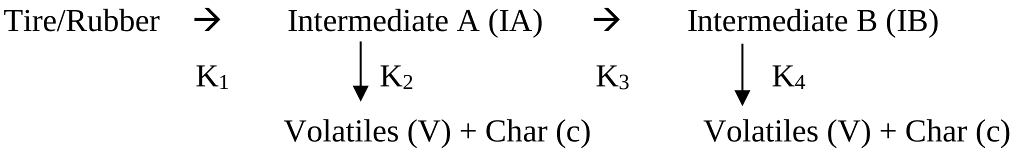
The model chosen to describe the pyrolysis reaction is based upon the work by [2] & [30]. The complete conversion process of tire/ reaction scheme is given below

Reaction 1: Rubber → Intermediate A (IA)

Reaction 2a: Intermediate A (IA) → Volatiles (V) + Char (C)

Reaction2b: Intermediate A (IA) → Intermediate B (IB)

Reaction 2c: Intermediate B (IB)→ Volatiles (V) + Char (c)



Kinetic properties	Reaction 1	Reaction 2a	Reaction 2b	Reaction 2c
Pre-exponential factor A(S^{-1})	4.17 $x10^6$	2.52 $x10^6$	9.96 $x10^6$	2.7 $x10^7$
Activation energy Ea (J/mol)	119.15$x10^3$	119.42$x10^3$	130.1$x10^3$	129 $x10^3$
Reaction enthalpy (J/Kg)	42.5$x10^3$	253.4$x10^3$	195.5$x10^3$	701.9$x10^3$

Table 4-3 The kinetic parameters at Temperature value 550 ^{o}C [30]

In this kinetic scheme made up of parallel reactions, the reaction constantsK_1, K2, K3 and K_4 are those corresponding to the primary reaction steps to give IA, Volatiles and char, IB and volatile and char from the intermediate lump.

Accordingly, on basis of the four lumps; a first order differential equations is outlined below

$$\left(\frac{dXR}{dt}\right) = -(K1)(XR) \tag{10}$$

$$\left(\frac{dXIA}{dt}\right) = (K1)(XR) - (K2)(XIA) - (K3)(XIA) \tag{11}$$

$$\left(\frac{dXIB}{dt}\right) = (K3)(XIA) - (K4)(XIB) \tag{12}$$

$$\left(\frac{dXV\&C}{dt}\right) = (K2)(XIA) + (K4)(XIB) \tag{13}$$

Where X_R, X_{IA}, X_{IB} and X_{VC} are the yields of each one of the lumps in the kinetic scheme shown in equation 10-13.

Furthermore, In order to find the estimated volume of the reactor, the kinetics of the processes must be determined with the use of the famous Arrhenius equation.

At this stage, it is required to recall equation (2) and the parametric values associated with the pyrolysis reactions, which were taken from the parameters, listed in table 4. It is estimated that the pyrolysis reaction occurring within the reaction is at 450-550 °C, implying the absolute temperature to 723 kelvin. The Gas constant is generally 8.314J/mol k.

For simplicity, the screw reactor is considered as a continuously stirred tank reactor by incorporating the general assumptions. These are

1. Continuous process: Uninterrupted sequence of operations in which the feed material must be introduced in order to maintain equilibrium conditions
2. Steady state
3. Agitation: Back mixing and facilitates heat transfer

The design equation can be referred from equation 9. Here under, a redefined and a practical design equation is used to calculate the total volume with the use of **Levenspiel plot** by considering the conversion rate.

By taking the tire conversion, X; the outlet flow rate can be analytically stated as

$$F_j = F_{jo} - F_{jo}.X \,, \qquad (14)$$

Where, $F_{jo}.X$ is the molar flow rate at which "j" is consumed within the system

In the same way, F_{jo}(Inlet molar flow rate) can be expressed as

$$F_{jo} = C_{Ao} .V_o \qquad (15)$$

Where, C_{Ao} is entering concentration (mol/dm^3) and V_o is volumetric flow rate (mass flow rate (8 kg/hr)/density (1100 kg/m^3)

$$Vo\ =\ (15\ kg/hr)/(1100\ kg/m3)$$

$$Vo\ =\ 1.36E-2\ m3/hr\ or\ 3.78E-6\ m3/sec$$

The rate of formation/ consumption $-r_j$ can be expressed as a function of rate of reaction and concentration

$$-r_j = k * C_A = K * C_{Ao} * (1-X) \qquad (16)$$

Substituting equation 16 into equation 9, the total volume of rector V can be expressed as

$$V = \left(\frac{Vo}{K}\right)\left[\frac{X}{1-X}\right] \qquad (17)$$

Given $–r_j$ as a function of conversion, $-r_j = f(X)$, one can size any type of reactor. This is done by constructing a Levenspiel Plot. F_{j0} / $-r_j$ or 1 / $-r_j$ as a function of X.

For F_{j0} / $-r_j$ vs. X, the volume of a CSTR is the rectangular shaded for the respective values are averagely taken after analytical manipulation by making the mass flow rate, conversion to differ and for various kinetic parameters illustrated in table 5, the Levenspiel Plot can be generated.

A Levenspiel plot is simply a curve where the conversion X is in the abscissa and Fjo/-rain the ordinate. The area (Fjo/-ra*X) under this plot, signifies the minimum reactor size/ volume for CSTR type reactors.

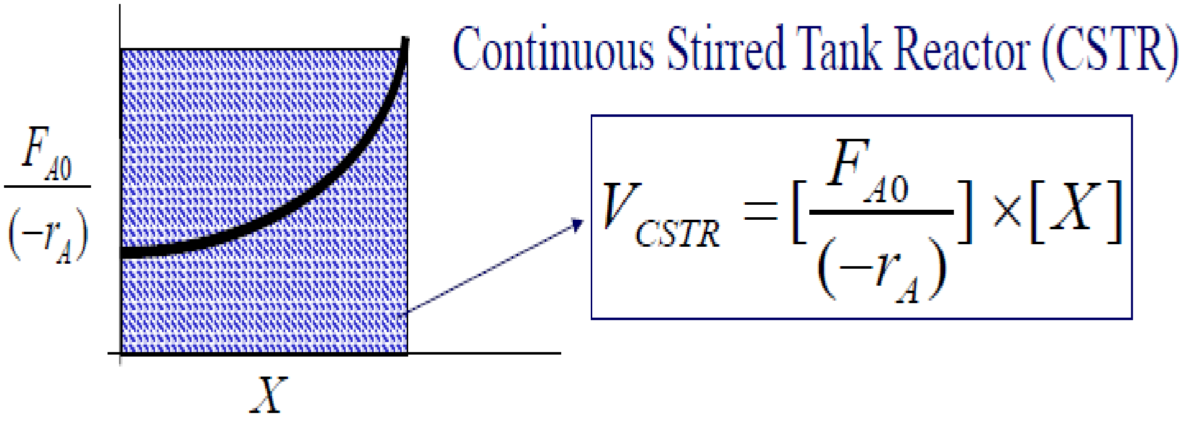


Figure 4-4 Levenspiel plot for reactor sizing

Therefore, plugging the kinetic values into the proposed kinetic model, the following tabular data can be acquired with an assumption that the minimum activation energy requirement and data acquisition is from [2]

mass flow rate [kg/hr]	Vol flow rate [m^3/sec]	E(KJ/mol)	A (1/s)	K	Xa	Vt [total volume, m^3]	Vt [total volume, lit]	residence time (s)	residence time in min	Fao/-ra
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.10	8.44E-05	8.44E-02	22.29	0.37	8.44E-04
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.20	1.90E-04	1.90E-01	50.15	0.84	9.50E-04
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.30	3.26E-04	3.26E-01	85.97	1.43	1.09E-03
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.40	5.07E-04	5.07E-01	133.74	2.23	1.27E-03
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.50	7.60E-04	7.60E-01	200.61	3.34	1.52E-03
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.60	1.14E-03	1.14E+00	300.91	5.02	1.90E-03
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.70	1.77E-03	1.77E+00	468.08	7.80	2.53E-03
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.80	3.04E-03	3.04E+00	802.42	13.37	3.80E-03
15.00	3.79E-06	8.93E+04	5.35E+3	4.98E-03	0.90	6.84E-03	6.84E+00	1805.45	30.09	7.60E-03

Table 4-4 Tabular data for construction of Levenspiel plot

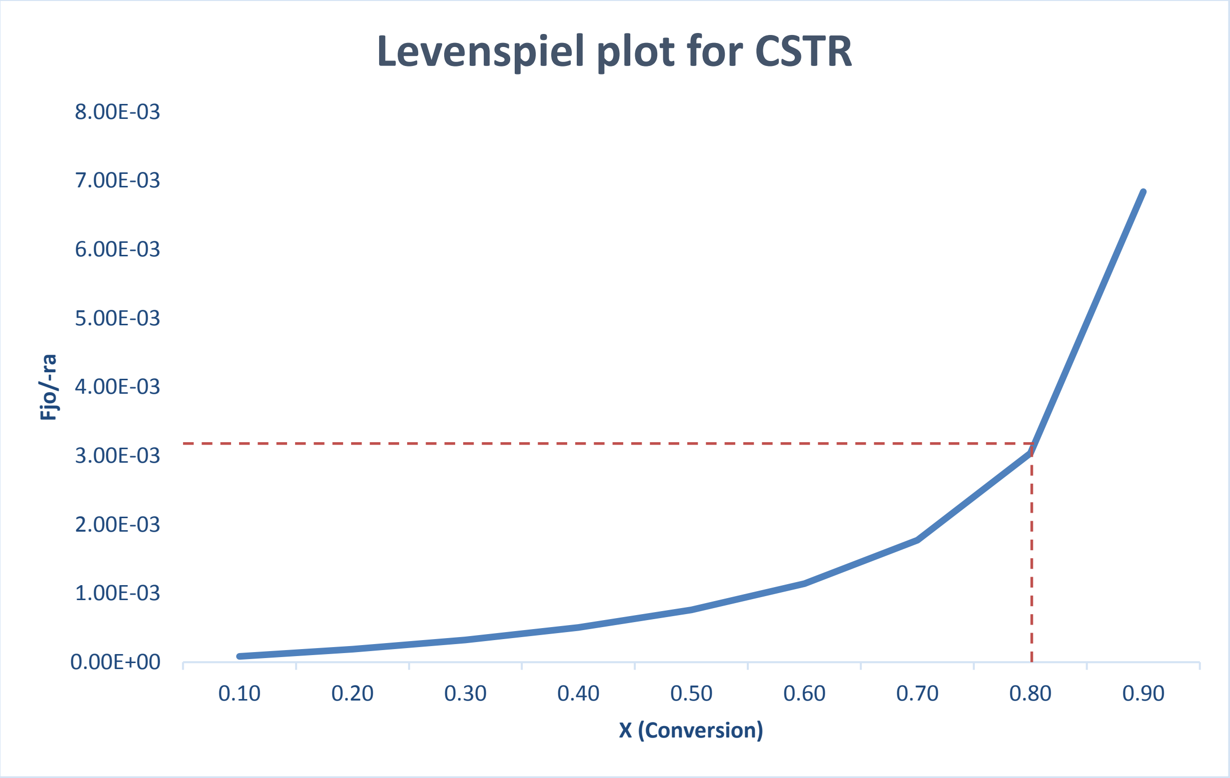


Figure 4-5 Calculated Levenspiel Plot for reactor sizing (area under Fjo/-ra Vs X)

At an estimated 80%-90% of conversion, the minimum reactor volume is found to be 3 to 6.84 liters. Therefore, the total volume was taken to be $\mathrm{Vt} = 0.007\ \mathrm{m}^{\wedge}3$ or 7 liters. (Minimum requirement). As the conversion rate approaches to 1 (i.e. X→ 1, the reactor volume V→ ∞)

4.3.5. Reactor residence time

It is a measure of time that tire particles will remain in the reactor, until they are converted into products (Volatile and chars) and ejected.

Therefore, the residence time is a ratio of volume of reactor to the volumetric flow rate

$$t(sec) = \left(\frac{Vt}{Vo}\right) \tag{21}$$

Therefore, average residence time @ 80% to 90% conversion rate is found to range 13 min - 30 min.

Usually, the solid residence time in auger reactors is determined by the length ans the rotational speed and pitch of the screw (Funk et al., 2017) [42].

4.3.6. Heat transfer and Energy requirement of the reactor

4.3.6.1. Particle size and Biot, Pyrolysis number correlation

The section 2.10 of the literature review discusses about the dimensionless quantity called Biot number, which gives simple index ratio of the heat transfer resistance inside of a body and at the surface of body.

Recalling Eq 6, the Biot number for the particle size of 5mm can be determined

$$Bi = (hL)/(K)$$

The thermo physical properties of tire rubber are

Parameter	Value	Reference
h (Film coefficient)	50 W/m^2 k	[30]
L (Characteristic Length/diameter _Particle size)	5 mm / 0.005 m	Measured

Parameter	Value	Reference
K (Thermal conductivity of tire)	0.38 W/mk	[30]
Density	1,100 kg/m^3	[30]
Cp	1,230 J/kgK	[30]

Table 4-5 Thermo-physical properties of tire

Accordingly, the Biot number is calculated as

$$Bi = (50\, w/m2\, k * 0.005)/(0.38\, W/m\, k)$$

Bi = 0.66

Therefore, a Biot number much smaller than unity represent thermally thin regime, i.e. heat conduction within the particle is lot faster than heat convection to the particle [41]. It’s possible to assume that the particle size of 5mm is nearly in isothermal state and can be used for tire pyrolysis without any adverse effect on the process.

Pyrolysis number, *py’* also provides the isothermal state and kinetic regime of the reduced particle size. As proposed in [41], a pyrolysis number much larger than unity, heat convection to the particle is a lot faster than chemical reactions taking place.

$$Py' \; cylindrical\; particles = \frac{h}{k.\rho.Cp.Lc} \tag{22}$$

Substituting the corresponding values,

$$Py' \; cylindrical\; particles = 19.94$$

Therefore, 19.94 is much larger figure than unity (1); so it can be concluded that the heat convection is lot faster.

4.3.6.2. Heat transfer and Energy requirement of screw reactor

In this study, the pretreatment of tires do not require any moisture drying unless size reduction. Therefore, the total energy requirement will be the heat supply required to make the reactor reach a pyrolysis temperature around 450-550 °C.

Due to the mixing and turbulent nature of the auger reactor, the following assumptions are made for the heat transfer model

i. Heat transfer takes place in axial direction and perpendicular to the reactor
ii. Material is considered as a continuum phase

The hat transfer equation for a control volume can generally be written as (in the presence of an axial temperature difference ΔT) shown below

$$\dot{q}(\dot{m}, T, x) = h(\dot{m}, T)A\Delta T + \dot{m}\int_{T1}^{T2} Cp\,(T)dt \qquad (23)$$

Where $\dot{q}$ is the hating rate to raise the material from T1 to T2, A is cross section ara of the reactor, $\dot{m}$ is the material mass flow rate, Cp is the specific heat capacity of the material, T is the absolute temperature in K and h is the heat transfer coefficient.

The reactor is set to be divided into three zones, namely ***Feeding***, ***reaction*** and ***by-product releasing zones*** where the direct heat supply is for reaction zone (Zone 2).

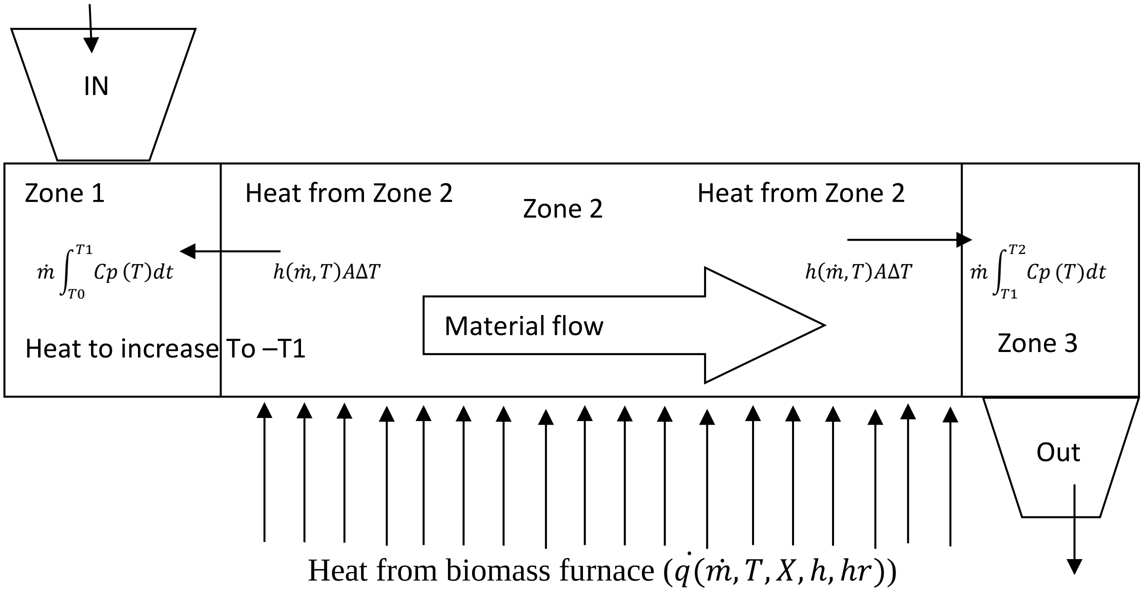


Figure 4-6 Heat analysis on the reactor

Zone 1: Heat from zone 2 ($h(\dot{m}, T)A\Delta T$) = Heat absorbed by the material flowing to raise its temperature from T0-T1 ($\dot{m}\int_{T0}^{T1} Cp\,(T)dt$)

Zone 3: Heat from zone 2 ($h(\dot{m},T)A\Delta T$) = Heat absorbed by the material flowing to raise its temperature from T1-T2 ($\dot{m}\int_{T1}^{T2} Cp\,(T)dt$)

A MATLAB simulation (see Appendix-A2) of the heat transfer scenario before the introduction of waste tire particles was performed and the main parameters used are;

- h (convection heat transfer coefficient @ the bottom of screw case[Zone 2]): 250 w/m^2 K (Forced convection – On the small scale pyrolysis plant, a blower is used to facilitate the convective heat transfer)
- h (convection heat transfer coefficient @ the side of screw case[Zone 1&3]): 25 w/m^{2}K
- k (Thermal conductivity of steel (screw case)) – 54 W/m K
- Cp (Specific heat) – 1.625 J/kg K
- T (temperature at the bottom of screw case) – 773.15 Kelvin
- Rho (density) = 7870 kg/m^3

N.B: The temperature variation along the X-direction is portrayed on the result section 6.2.

The combined heat transfer within the biomass furnace to the surface of the reactor was also calculated on Appendix A-4 as per the direction portrayed by [49] and the results were;

- Combined Heat transfer per unit length q”(conv+rad) = 152.47 KW/m
- The heat loss from external surface per unit length q”(loss) = 974.14 W/m

For the input fuel, charcoal is used for ease of accessibility and heat supply for extended period due to the carbonization effect. Therefore, to determine the energy requirement/fuel input to raise the temperature of the tire material to the required pyrolysis temperature

Firstly, the energy content of the tire needs to be known, heat energy is given as

$$Q = mc\Delta T \qquad (24)$$

Where Q is heat energy (watt, J/s), $\dot{m}$ is Mass of material (kg), C Specific heat (J/Kg.k), ΔT change in temperature

$\dot{m}$ = 15 kg/hr ~ 0.00416 kg/s (intended maximum mass flow rate)

C = 1,230 J/kg.k [30]

ΔT = 525 kelvin

Where $T_{initial}$ = 25 °C (298.15 k) and T_{final} (pyrolysis temp) = 550 °C (823.15 K)

Therefore: $Q = 0.00416 \frac{kg}{s} * 1230 \frac{J}{kgk} * 525k$

$\mathrm{Q} = 2{,}690.625 \mathrm{~J/s}$ (2.69 kW)

In order to deliver *q=2.7KW* energy to the system, the quantity of fuel requirement can be calculated by making alterations to Equation (24)

$$\dot{m} = q/C\Delta T \qquad (25)$$

The specific hat capacity of locally available materials

Type of material	Specific heat capacity [KJ/(kg K)	Reference
Wood, oak	2	[43]
Charcoal	1	[43]
Fiber board, light	2.5	[43]
Fiber hardboard	2.1	[43]

Table 4-6 Specific heat capacity of selected Biomass

Taking the average specific heat capacity as 1.9 KJ/Kg K, the required mass flow rate for input fuel becomes

$$\dot{m} = (2.69\ KJ/s)\ /(1.9\ KJ/\ Kg\ K)(525\ K)$$

$$\dot{m} = 2.69\ x\ 10 - 3\ Kg/s\ or\ 9.96\ Kg/hr\ of\ fuel$$

4.3.6.3. Energy balance on the pyrolysis reactor

With regard to the energy balance within the reactor, heat flow and enthalpy flows are expected to occur. These are the enthalpy introduced by the feed stock ($H_{tire,in}$), input energy by means of burning of biomass fuels (Q_{in}), associated flue gas existing the system (H_{out}) and the heat losses by the reactor side walls, top and bottom (Q_{loss}). The Enthalpy flow Hp, is consumed by the tire particles in the pyrolysis process, the resulting energy balance becomes

$$Hp = Q_{in} + H_{tire,\,in} - Q_{loss} - H_{out} \qquad (26)$$

4.3.6.4. Conservation of mass (Mathematical Modeling)

The development of the mass transfer model for waste tire pyrolysis is resented here, where the general modeling technique is adopted from [46]. A simplifying assumption was introduced to reduce the complexity of the model.

A schematic of tire chips in which 1D-model was considered for the mass transfer

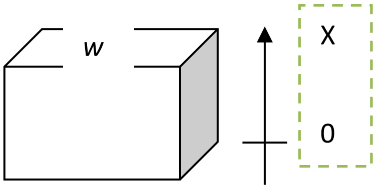


Figure 4-7 Tire particle

To derive the mass balance, the concentration of species *i* or density of species as the mass per unit volume of space, $[Ci] = kg/m^3$

The reaction rate r_i, implies the production of species *i* per unit volume per unit time is given by $[r_i] = Kg/m^3s$

Assumption: Species *i* is transported in the x-direction perpendicular to the top surface (across the area w) and taking the mass balance across the section Δx gives with a differential time t;

$$W\Delta x C_i \big|_{(t+\Delta t)} - W\Delta x C_i \big|_{t} = \Delta t W(J \big|_{x} + u_i C_i \big|_{x}) - \Delta t W(J \big|_{(x+\Delta x)} + u_i C_i \big|_{x+\Delta x)}) + W\Delta x r_i \Delta t \qquad (27)$$

Where u_i is the species flow velocity and J is the mass transfer flux of species *i*. W is the surface of the tire chi through which the ass transfer takes place (the mass loss is assumed to be uniform at any direction)

Dividing equation (27) by $\Delta x\,\Delta t$, and taking the limit Δx → 0, Δt → 0

$$\frac{\partial Ci}{\partial t} = \frac{\partial J}{\partial x} + \frac{\partial (UiCi)}{\partial x} + ri \qquad (28)$$

Equation 27, is the governing mass transfer equation for all species generated and transported through the volume.

4.4. Process design and Analysis

As per the technical information obtained in a global search by Galaxy, Inc., Tire pyrolysis activities are classified according to several criteria:

- Method of heat addition
- Material handling
- Reactor type
- Feed preparation

4.4.1. Functional Specifications and requirements

The intended Auger reactor type pyrolysis plant uses various types of tyres as a feed stock with a range of small to heavy duty vehicles to recover the energy contained with a renowned process pyrolysis.

The core process, i.e pyrolysis of waste tyre will follow heuristic procedures adopted from the reviewed literatures to get acceptable product features of 40% solid fractions and 60% of volatile fractions comprising of liquid and gasses.

Before beginning to design a reactor, a desired metrics must be laid out that ensure the pyrolysis reactor both reacts fast, isothermally and continuously. The target metrics are

Parameters	**Measurement/Required performance level**
Feed stock characteristics	
Type of feed stock	Shredded tire, Crushed tire
Feed rate	8-15 kg/hr
Particle size range	~5 mm

Parameters	**Measurement/Required performance level**
Elemental composition in wt.%	82.4 wt.% Carbon, 7.639 wt.% Hydrogen, 0.282 wt.% Nitrogen, 0.923 wt.% sulfur and 8.69 wt.% oxygen
Operating procedures	
Heating rate	3-5 ˚c
Time held at intermediate and final temperature	15-30 min
Reactor temperature	350-500 ˚c
Final temperature/ Temperature limit	500-550 ˚c
Residence time	< 30 min
Min run time	< 1hr
Cycle time	15 min for 3.5 kg of tire input
Capacity of process plant	8-15 kg/hr
Source of heat	Charcoal/Biomass
Output	60% of volatile fraction & 40% solid fraction

Table 4-7 Functional specification

4.4.2. Component design

4.4.2.1. Design considerations of Screw conveyor and manufacturing

On usual physical phenomena, screw conveyors are employed for transportation of pulverized, granular and small size lumpy bulk materials to relatively short distance. The movement of materials is forced through the trough by rotating screw, which is formed by helical blade attached to the drive shaft [44].

The function of the screw is to provide sufficient mixing and to convey the tire particles through the reactor as it is decomposed, so it can be operated in a continuous process. The design of the screw is very important for mixing and characterization of the granular flow [45].

The required capacity of the pyrolysis plant is to process 15 kg of waste tires within an hour and the recommended trough loading percentage is planned to occupy 30% of the trough is solid state to allow the produced gases/volatiles to occupy the 70% of the trough.

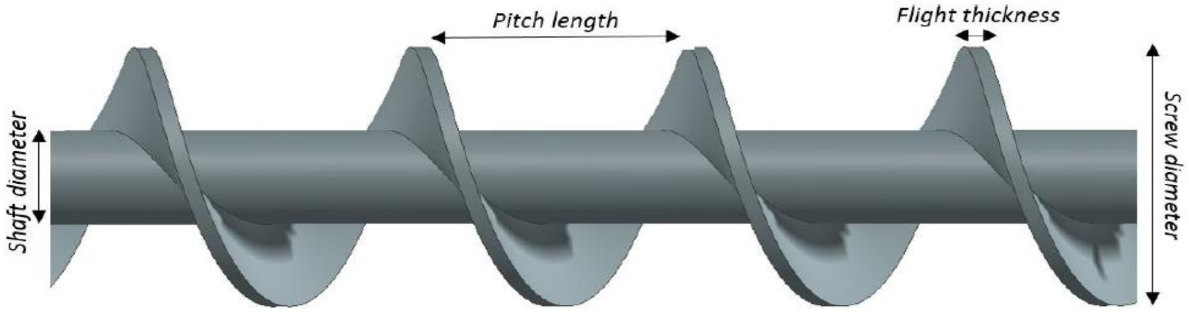


Figure 4-8 Characteristic dimensions of a screw [45]

The essential parameters to be established in the design or selection of a screw conveyor for a given application are the screw size and its rotational speed. A detailed design and practical development for manufacturing purposes are portrayed on Appendix A-3

Parameters	Values	Assumption
Screw diameter (outer)	190 mm	Twelve times the size of lumps (materials) [44]
Shaft diameter	60 mm	Hollow shaft made of stainless steel-Light shaft load
Screw pitch	190 mm	Standard type-Full pitch
Radial clearance	12 mm	1.75 to 3 times the size of largest lump
Length	2 m	
RPM	10-30	Calculated
Trough and screw flights thickness	3 mm	Material selection:
Power requirement	1.5 KW	Availability on market
Helix type	Left hand	
Support type		Suspended by end bearings

Table 4-8 Screw conveyor characteristics

4.4.3. Product yield and thermal Efficiency calculations

In order to determine the yields of the products, the amounts of char and pyro-oil obtained was quantified by weighting the corresponding unit before and after each experiment. The exhausted gases mass was calculated by difference.

Pyro oil and char yields can be calculated as [42]

$$Yield\ pyro\ oil\ (\%W/W)\ =\left(\frac{moil}{mf}\right)x100 \quad (29)$$

$$Yield\ char\ (\%W/W)\ =\left(\frac{mchar}{mf}\right)x100 \quad (30)$$

$$Yield\ gas\ (\%W/W)\ =\left(\frac{mf-mchar-moil}{mf}\right)x100 \quad (31)$$

$$Yield\ liquid\ organic\ (\%W/W)\ =\left(\frac{100-water\ content}{100xyield\ pyro\ oil}\right)x100 \quad (32)$$

Where, m_{oil} is mass of pyro-oil, m_{char} is the mass of the char by product, m_f is the initial mass of scrap/waste tire

Furthermore, to product yield calculation, it is also convenient to estimate separately the thermal conversion efficiency of the tire pyrolyzed mass in each one of their respective products (char, pyro-oil & gas) [57], as depicted on Eqs 33 & 34.

$$\eta char\ =\frac{mchar\ x\ HHV\ char}{mtire\ x\ HHV\ tire}*100 \quad (33)$$

$$\eta pyro-oil\ =\frac{mpyro-oil\ x\ HHV\ pyro-oil}{mtire\ x\ HHV\ tire}*100 \quad (34)$$

$$\eta Gas\ =\frac{mgas\ x\ HHV\ gas}{mtire\ x\ HHV\ tire}*100 \quad (35)$$

4.5. Solid modeling and fabrication of Screw reactor Key components

Solid models for the screw reactor were developed. These efforts were primarily focused on determining geometry and part orientation for key subsystems, namely the screw conveyor (integrated feed and reactor system), biomass furnace and insulation system.

The hopper is sized so as have sufficient volume to run for two hours (Nearly 25 kilograms). The screw casing and screw conveyer has a net length of 2 m to have a control over residence time, ensure an adequate hat transfer is achieved and the feedstock material fully converted into the intended by products (Volatile and char).

The biomass furnace which is enclosed by a 60mm thick insulation , with an insulation and heat absorbing material "BIOMASS ASH" is modeled to ensure the minimum heat transfer towards the outside/ Ambient temperature.

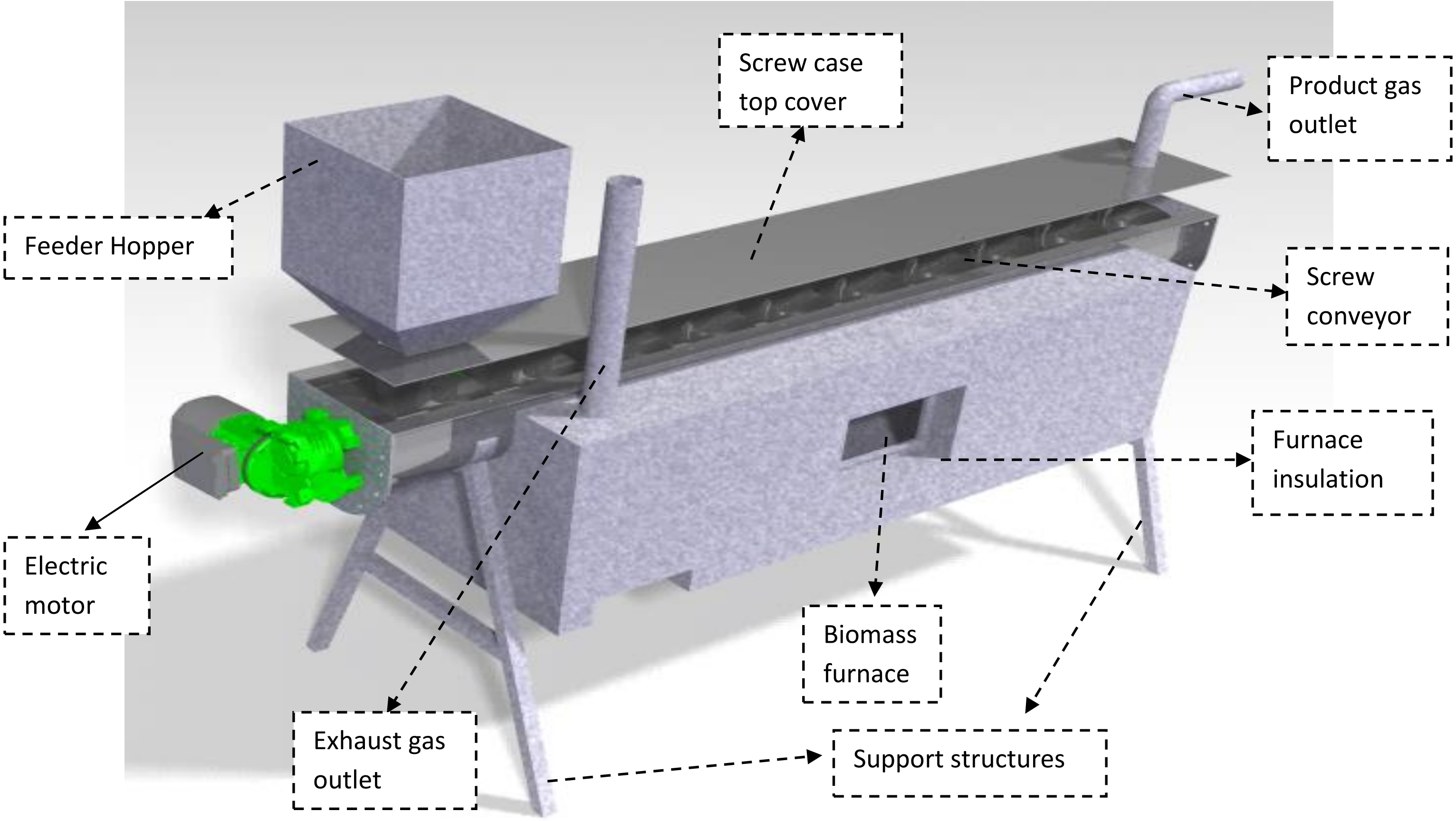


Figure 4-9 Solid modeling of screw reactor

A motor coupled with an inverter control, Variable frequency drive is directly, or by use of V-belt, the rotational power is transferred to the screw conveyor shaft. The inverter is used to control the electric motor speed /RPM (Revolution per minute) with the range of 10 to 20 RPM.

CHAPTER FIVE

5. EXPERIMENTAL INVESTIGATION OF THE PILOT PYROLYSIS PLANT

5.1. Experimental set up and objective

The objective of the experiment is to perform staged temperature pyrolysis of waste tire in a continuous process to condense volatile matters, trap and recalculate the non-condensable gases to the combustion system and acquire the byproduct of char on solid state. The fabricated screw reactor and its components are portrayed hereunder

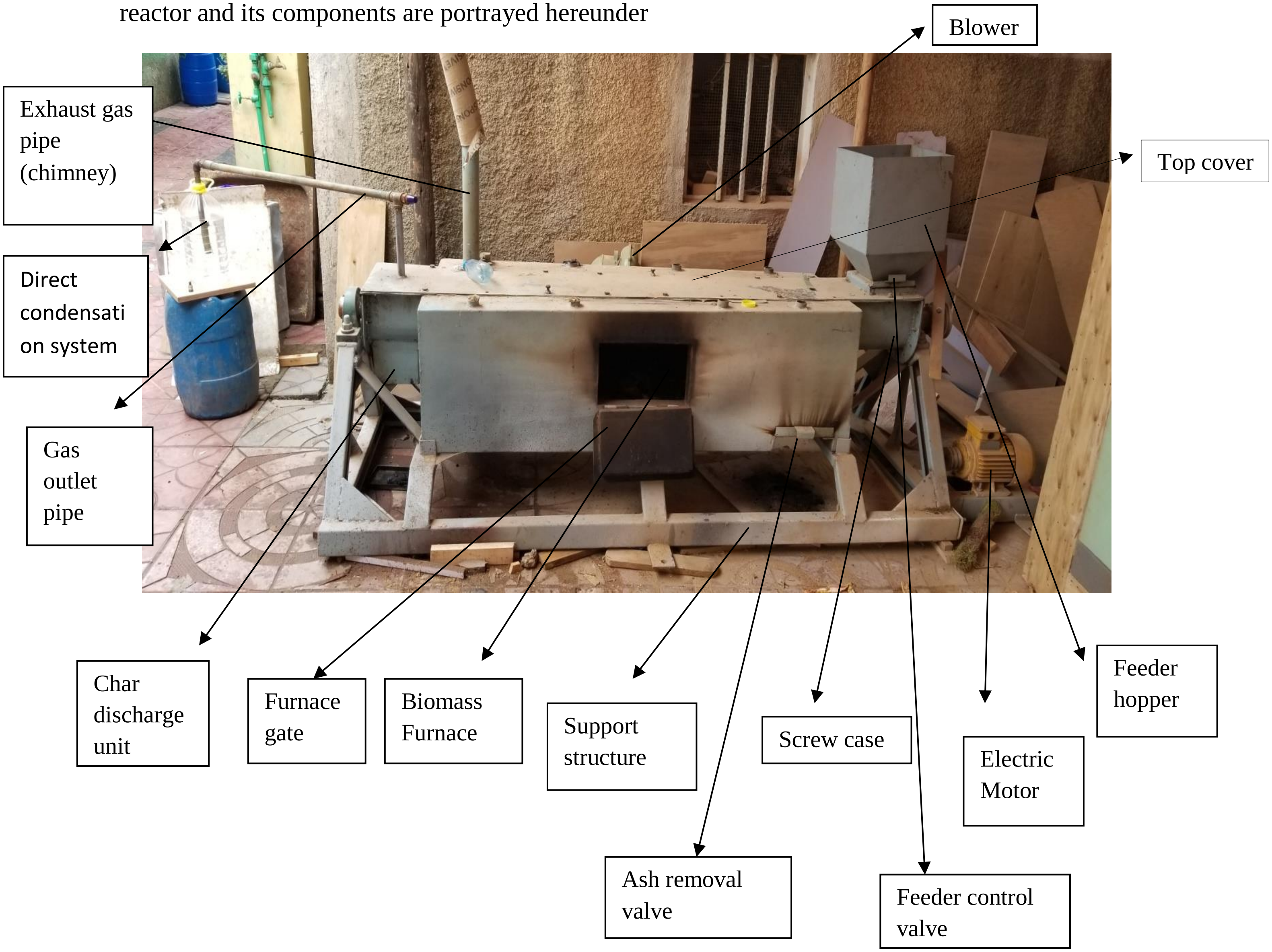


Figure 5-1 Fabricated Screw reactor

The construction of pilot continuous pyrolysis reactor made for specific study purpose comprises the following elements and principles

- Hopper with side valve
- Ac motor controlled by an Inverter (Variable frequency drive)
- Screw reactor with a span of 2m
- A combustion chamber assisted by a blower
- Non-hazardous operation, simple, Efficient
- Construction materials are to be locally available and durable

5.2. Procedure

For each experimental run, the conditions such as initial waste tire mass, reactor temperature and velocity of screw are defined at the start.

In operation, the crushed waste tire is placed in the feeder hopper while the required amount of charcoal and biomass is fed in biomass furnace and fired up with a sprinkle of gas. After some time (depending on the firing mechanism and combustion efficiency), the inner part of the screw reactor is made to reach to a pyrolysis temperature of 500 °C**.** After assuring the reactor reaches a steady temperature, the material was loaded on the feeder hopper.

The feedstock material can then be fed into the reactor by metering the flow using the feeder control valve and by simultaneous operation of the screw rotation (positive rotation to counter clockwise direction), and then the shredded tire particles make their way to the heated screw case by avalanching effect caused by the screw flights linearly advancing motions.

On the first test run, the condenser unit was left unattached with the system to make sure the desired products are being produced in product gas collection pipe.

Conditions used in the first experimental run are described below:

- The three zones of screw reactor were maintained on three heat zones with a temperature difference ranging 50-100 Kelvin's. The temperature of the first heating section of zone 1 & 3 (around 690-700 Kelvin's) and Zone 2 around 750-760 kelvins. Matlab code can be referred in Appendix A.2

- The screw were operated at a speed of < 10 RPM
- The gasket used in the screw casing and top cover and side plates was an Asbestos steel reinforced gasket which has the capacity to withstand a temperature of 400-500 °C
- The reactor was run for 15 minutes and sample of char were collected and the produced gases rising through the vertical pipe of gas outlet were detected by burning it freely as shown on the figure

Figure 5-2 Gas production indication on first run

5.3. Running the equipment: Condition and variable & Data collection: Output

Pyrolysis condition: In each experiment, 3.5 kg of scrap tire was fed into the reactor with an assumption of the residence time to be approximately 15-20 min. Subsequently, the reactor is heated at a heating rate of 3-5 °C until the desired temperature (500-550 °C) reached, and then hold it for 15-30 min, if require it can be run for hours. The produced volatile matters are expected to leave the reactor naturally with moderate assistant from the screw rotation; no carrier gas also vacuum pump is used for this study.

CHAPTER SIX

6. RESULT AND DISCUSSION

6.1. Kinetic Modelling result

The equations (10-13) presented in chapter 4, were solved in MATLAB using an ordinary differential equation (ODE) 23s solver (the MATLAB code can be referred in Appendix A.1), where such solvers in MATLAB are used to solve differential equations with a stiff problem type.

The result show that tire rubber is broken down on a relaxed manner and about 10 minutes, all the tire rubber compounds and intermediate lumps degrades into volatile and char (complete conversion). The conversion of both intermediate lumps and volatiles, chars begis when the majority of tire has been broken down.

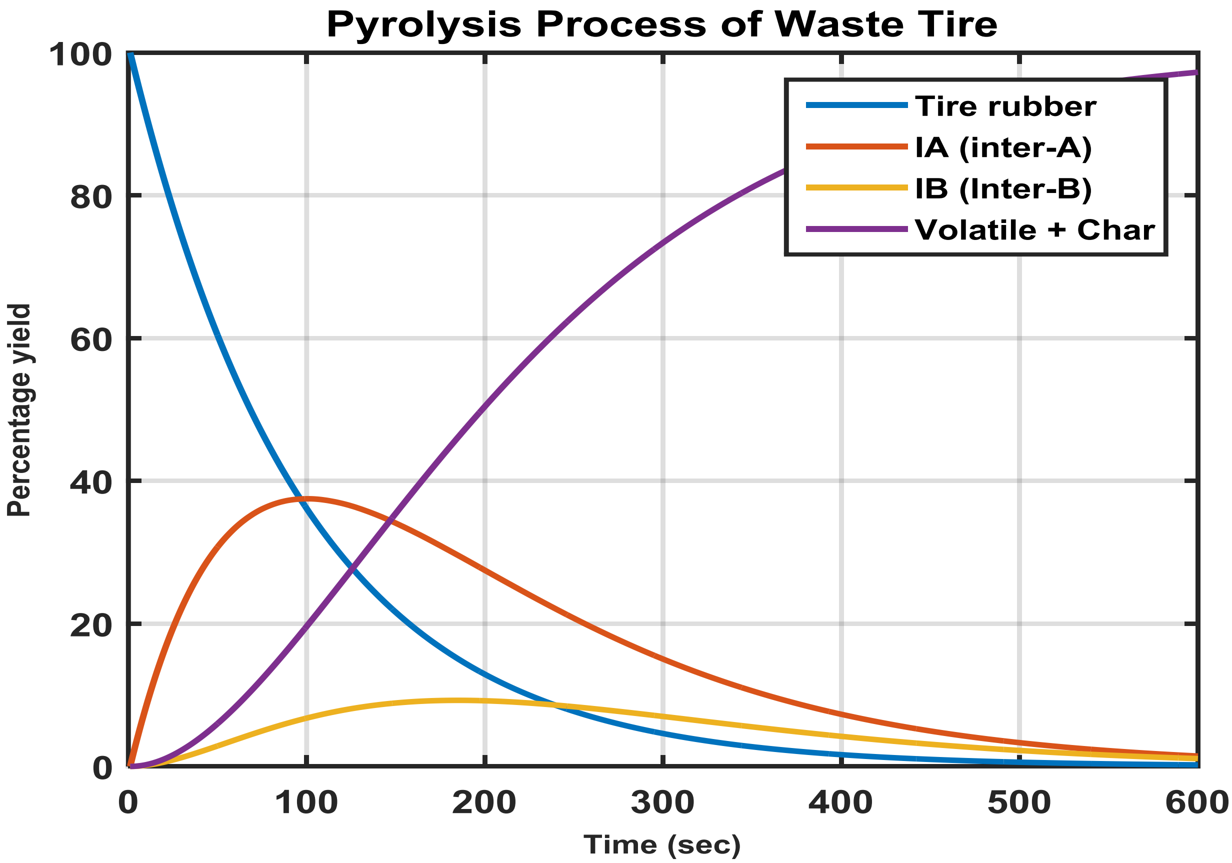


Figure 6-1 MATLAB Simulation of Pyrolysis of Tire

The above study is only valid for 550 ^{o}c and uses the assumption that no pyrolysis takes place prior to temperature reaching at 550 ^{o}c. It is also assumed that the temperature & reaction constant are constant throughout the duration of the pyrolysis process.

6.2. Temperature profiles (Variations)

In order to minimize the heat loses and create the drying effect on the inlet side, the ends of the reactor were kept isolated from the biomass furnace. It's expected that heat transfer through conduction to occur.

As discussed on section 4.3.6.2, the result of MATLAB simulation is portrayed on figure 6.2

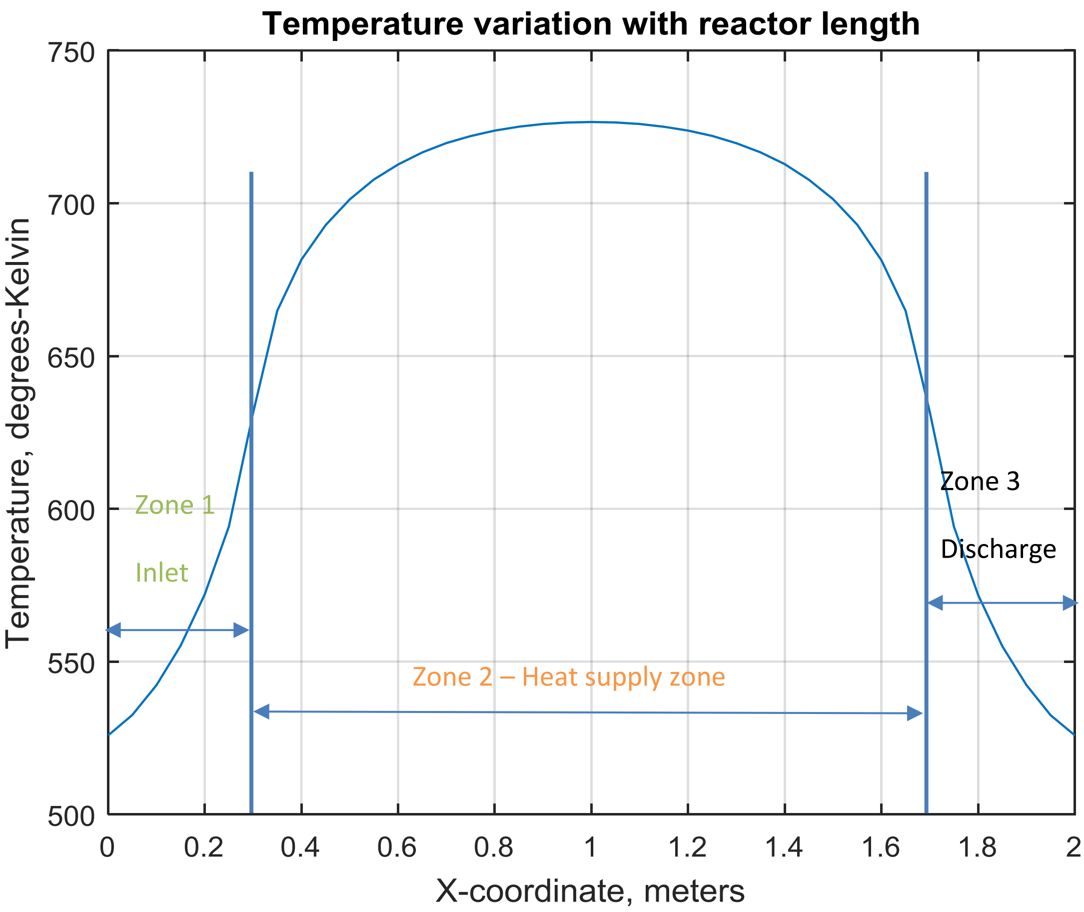


Figure 6-2 Temperature variations across the reactor length

On the experimental run, the typical temperature profile was recorded with the use of Infrared thermometer (FLUKE 568 IR THERMOMETER). The reactor temperature increases quickly until attain the desired pyrolysis temperature (500°C) and after about 45 minutes, it remains constant. As a result, reactor and other temperatures increases progressively along time ("Transient") until a steady-state condition is achieved (refer figure 6.3.)

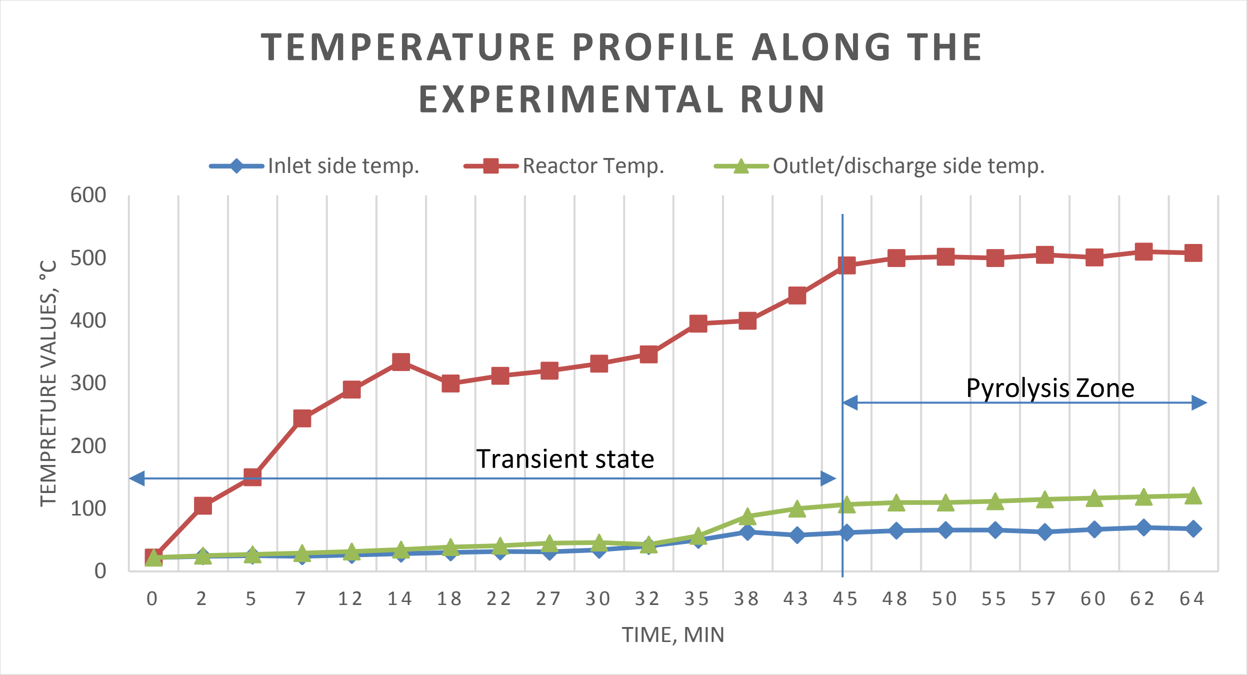


Figure 6-3 Temperature profile along the experimental run

6.3. Experiment results & Reproducibility

Pyrolysis products: In each experiment, the liquid and char yields were determined by weighing them after each experiment. The gas and aromatic yields was calculated by difference. The experimental runs were performed at least in a duplicate order to obtain a more reliable results.

Leakage of volatile matters at the connection points, ineffective condensation system are the main limitations of this experimental study which sabotage the whole test and the repeatability of the measurement.

	First run	**Second run**	**Third run**
Temp range	**450-512 °C**	**330-412 °C**	**432-510 °C**
Heat rate	**5.08 °C/min**	**7.3 °C/min**	**4.3 °C/min**
Yield (wt. %)			
Pyro-oil	**-**	**1.56**	**2.4**
Gas	**35.56**	**38.64**	**43.4**
Char	**64.43**	**59.8**	**54.2**

Table 6-1 Yields of pyrolysis products with the reaction temperature

Figure 6-4 Product Yields in wt. %

As can be seen from the product yield data, liquid yield is almost insignificant due to the poor condensation system utilized i.e. direct condensation. On the feedstock analysis, tires have 62.2 wt. % of volatile content which can be retrieved as gas and liquid.

It’s also observed that, the deficient separation of products instead of a rapid removal of char also decreased the formation of pyro-oil. In all the experimental runs, a visible portion of hot vapor was trapped in the discharge unit and kept in direct contact with char before it is sent to the direct condensation system.

In a more clear and concise words, not utilizing or creating an inert atmosphere within the reactor, the low heating rate in the reaction, leakage problems, ineffective condensation system and unable to separate the char products with the hot vapors in a screw configuration were the main experimental justification for the low pyro-oil yields.

As [12] describes a pyro-oil, the gathered oil has a dark-brownish color with an intense aroma resembling to a crude oil with high viscous feature with a calorific value of 44 MJ/KG energy content depending on the tire composition and process condition. This pyro-oil has a higher calorific value than waste tire from which is recovered. It also shows similar properties to those of light fuel liquid with similar calorific value and Sulphur content [9], which encourages for us of as a replacement for conventional liquid fuels.

Sulphur compounds formation in the pyro-oil is due to the thermal degradation of additives such as vulcanization agents and accelerators added during the tire manufacturing process [9].

Figure 6-5 Pyro-oil/Scrap tire oil, Gas fractions with visible oil condensates and flammability test of pyro oil (left to right)

6.4. Effects of operating conditions (Sensitivity Analysis)

The rotating frequency of a screw reactor is the main operating parameter, which have a direct influence on particles residence time in the reactor. During the experiment, it's been noticed that higher screw speed leads to shorter residence time. Moreover, with increasing rotational speed; more particles taken up and throw over the shaft that facilitates the mixing and effective heat transfer. The adverse effect of high rotational speed is, the fast conveying/rushing of tire particles to the exit outlet without achieving the required conversion.

For a relatively higher velocity, the waste tire particles partially pyrolyzed as consequence of minimum contact time of particles with the heated wall (reactor wall). In addition, a much larger granular size beyond 5mm were used to witness the thermal degradation but it clear to notice that, partial pyrolysis dominates for irregular lump size.

For an induction motor with 1.5 KW, operating at 50 HZ with a RPM close to 1,430 controlled by a variable frequency drive, the starting frequency is 0.16 HZ (10 RPM) and can exceed to 0.33 HZ.

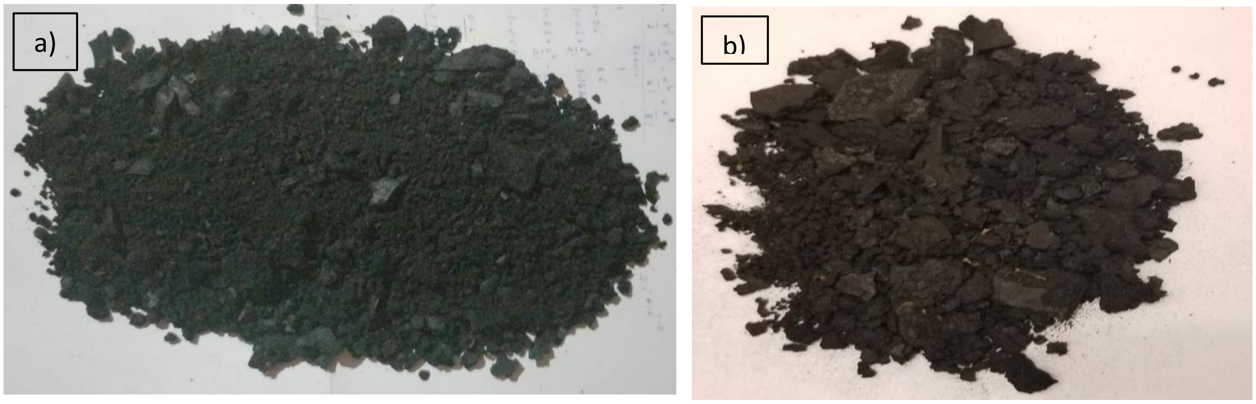


Figure 6-6 Sample of char a) 5mm particles with 10 RPM B) > 5mm particles (granules) with 28 RPM

6.5. Product characteristics and Thermal efficiency of pyrolysis reaction production

The byproducts characteristics (Pyrolytic oil, Pyrolytic carbon black (char) and syngas) were analyzed after gathering the results from Geological survey of Ethiopia. The results are portrayed in table 6.2 and 6.3.

6.5.1. Pyrolytic carbon black (Char)

Parameters	**Char - Experiment**
Lower Heating Value (MJ/Kg)	33.14
Proximate analysis	
Moisture Content	2.58
Volatile matter	10.65
Fixed carbon	73.11
Ash	13.67

Table 6-2 Properties of pyrolytic carbon black

6.5.2. Elemental analysis of Pyrolytic oil

The elemental analysis of the produced pyrolysis oil is determined experimentally as shown in Table below. Based the result the carbon content of the tire pyrolysis (wt. %) is 85.9 % that is comparable to diesel (87.1 %). Besides, the Calorific value is the oil is 46.35 MJ/kg that is higher than the diesel oil. Based on the result, the produced tire pyrolysis oil can be a replacement diesel if appropriate cleaning systems are used.

Property	**Tire Pyrolysis Oil (this study)**	**Diesel Oil [12]**
Lower heating Value (MJ/kg)	46.35	46
Density @ 30 ^{O}C (g/cc)	0.924	0.78
Kinematic Viscosity @ 40 ^{O}C	2.69	3.3
Flash Point (^{O}C)	68	75
Water Content , Moisture vol%	-	0.05
Ultimate Analysis (wt. %)		
C	85.9	87.1
H	7.99	12.8
N	0.36	0.05
S	1.05	0.9
O	2.25	-
Ash	2.45	0.01

Table 6-3 Pyrolytic oil characteristics

6.5.3. Pyrolytic gas(Syngas)

Gas obtained from the pyrolysis of waste tires is named pyrolytic gas, pyro-gas or syngas. It can range from a few percent to more than ten percent of the products depending on the technology used and the process conditions. It has a high heating value, up to about 84 MJ/Nm^3 or 42 MJ/kg [58].

6.5.4. Thermal Efficiency of pyrolysis reaction production

Thermal conversion efficiency of the waste tire pyrolyzed mass in each one of their products (char, pyro-oil & syngas) of the experiment was estimated by using equations (33, 34 & 35) portrayed in chapter 4, section 4.4.3, the thermal efficiency can be calculated with the use of heating value parameters from section 6.5. The results are shown in table 6.4.

Detailed calculations can be referred from appendix A-5.

Thermal efficiency (η)	This study	Data reference [17] & calculated
η_{char}	69.08%	40.57%
$\eta_{Pyro\text{-}oil}$	4.27%	62.25%
η_{syngas}	70.1%	22.7%

Table 6-4 Thermal efficiency of pyrolysis reaction products

The thermal efficiency presented in table 6.4 shows variations due to the mass yields and heating values of products. Therefore, it can be observed that the greater heating value of products from the waste tire (around 26 MJ/Kg) makes the individual thermal conversion applicable for commercial use.

6.6. Related developed work

The design validation is carried out by comparing the basic design parameters with a practical applications suggested by prior researchers. The basic parameters are: Screw diameter, pitch and length of screw, mass flow rate and residence time. It has been tried to compare these main parameters on [42].

In a study by Ferreira et al. (2015), pyrolysis of Medium Density Fiberboard (MDF) wastes was carried out in a semi-continuous pilot screw reactor. Screw conveyor is 2 m long, 195 mm in diameter and 195 mm in pitch. Experimental tests were performed at two temperatures (450 and 600 °C) monitored at the entrance of the char collector. Pyrolysis reactions were carried out under slightly negative pressure produced by a centrifugal fan installed on top of the bio-oil separator and no carrier gas was used. Three solid residence times were tested (9, 15 and 34 min). The maximum bio-oil yield (40 %) was obtained at 600 °C for the longer residence time as bio-char yield was 17.3 %. The highest bio-char yield (39.7%) was obtained with the longest residence time at 450 °C [42]. Therefore, the comparable screw conveyor dimensions, feedstock feed rate, reactor length also assures that the overall reactor configuration is suitable for pyrolysis processes.

CHAPTER SEVEN

7. CONCLUSION AND RECOMMENDATION

7.1. Conclusion

Present study has provided a comprehensive knowledge on existing continuous pyrolysis reactor technology, feed stock preparation, feeding system, modeling & fabrication of screw reactor, kinetic modeling & simulation and effect of operating parameters on product recovery.

In this study, a fraction of scrap tires were pyrolyzed in a screw reactor at various control variables like temperature, heat rate, particle size and rotation of screw. The yield of gas increased with increasing reaction temperature; whereas the liquid fractions decreased due to the secondary reactions. The screw/auger reactor used in this study operates at 450-550 °C on continuous mode where all the product yield measurements were taken. The yields pyro oil, char and gas obtained were quantified. Pyro-oil yields were 2.4 wt. %, gas 43.4 wt. % and char 54.2 wt. %.

The particle size of 5mm was found to be suitable for pyrolysis reaction of waste tires as per the validations made through biot and pyrolysis number. It is found that, particle size of 5mm is nearly in isothermal state and can be used for tire pyrolysis without any adverse effect on the process and the heat convection to the particle is also a lot faster than chemical reactions taking place.

On this master's thesis, only a limited amount of parameters was tested for their sensitivity towards reaction temperature, heat rate, screw velocity and particle size. The modelling and experimental results were found to have a disagreement on the results, especially on the pyro-oil yield due to the inbuilt technical issue on condenser selection. In view of the screw reactor, it is found that such reactor configuration is suitable for tires with larger lump sizes for its better thermal efficiency, continuous operation, moderate requirement of carrier gas and easy product removal system. However, the occurred lower pyro-oil yield resulted from the use of direct condensation system which leads to final conclusion that a direct condensation system is not suitable for continuous pyrolysis plant. In general, the screw reactor configuration in pyrolysis of waste tire have potential to recover high valued by products in an efficient manner.

7.2. Recommendation and Future work

So far, the motivations and produced results invites other to work more on advance level by resolving the current issues. The research was fully funded by the researcher and the limitations to access proper instrumentations for measurement shows uncertainty on the presented results. More future work can focus on a more detailed investigation of model sensitivity towards various operational conditions (wall temperature, screw rotating frequency, degree of filling…), physical properties (size, density, moisture content, heat capacity…) and model parameters (packing limit, drag model, heat transfer model, etc.)

In addition, by adopting a purification system, the obtained pyrolysis oil (fuel) could be utilized in diesel generators, vehicles such as tractors and passenger vehicles such as cars. The fuel has to be refined at the industrial establishments, based on the results of which small-scale industry can be established.

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APPENDIX

A.1- MATLAB code for Determination of Product yield of tire decomposition

```
% This program is adopted from [36] but major corrections were done to suit for tire decomposition

% the method used for kinetic modelling is the "single step independent reaction model"
clearall;
closeall;
clc;
mass = 8;        % total input mass, kg
MM = 68.12;          % molecular mass of isoprene Isobutylene rubbers mol/g
N = (mass*1000)/MM;

C0 = [N 0 0 0]; % Initial Condition, e.g. total amount  of moles
time = [1:600];        % seconds

[t,x] = ode23s(@reaction,time,C0);

x1 = (100*x)/(N);

plot(time,x1,'LineWidth',2);
axis([0,600,0,100])
title('Pyrolysis Process of Waste Tire');
xlabel('Time (sec)','FontSize',10,'FontWeight', 'bold');
ylabel('Percentage yield','FontSize',10,'FontWeight','bold');
legend('Tire rubber','IA','IB', 'Volatile + Char');
legend('Location','northeast');
set(gca,'FontSize',12,'FontWeight','bold','linewidth',1.5)
holdon

% The function that containts the ODEs.

dcdt=zeros(4,1);    % This defines the number of equations to be solved

% Defining the frequency factors (A)[1/s] and
% activation energy [Kj/mol] to get the K (reaction constant) values (reaction constants).
%A_1 = 51.7;       % Rxn_1 (TA--> volatiles (V) + Char (C))
A_2 = 4.17e6;     % Rxn_2 (Rubber-->Intermideate A (IA))
A_3 = 2.52e6;     % Rxn_3a (Intermediate A (IA)--> Volatiles (V) + Char(C))
A_4 = 9.96e6;     % Rxn_3b (Intermediate A (IA)-->Intermideate B (IB))
A_5 = 2.70e7;     % Rxn_3c (Intermediate B (IB)--> Volatiles (V) + Char(C))

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%E_1 = 61.63e3;         % Rxn_1
E_2 = 119.15e3;        % Rxn_2
E_3 = 119.42e3;        % Rxn_3a
```

```
E_4 = 130.1e3;         % Rxn_3b
E_5 = 129.1e3;         % Rxn_3c

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
T = 723; % [k] 500 degcel
R = 8.3144; % [J/mol.K]
%K_1 = A_1*exp((-E_1)/(R*T)); % Rxn_1
K_2 = A_2*exp((-E_2)/(R*T)); % Rxn_2
K_3 = A_3*exp((-E_3)/(R*T)); % Rxn_3a
K_4 = A_4*exp((-E_4)/(R*T)); % Rxn_3b
K_5 = A_5*exp((-E_5)/(R*T)); % Rxn_3c

%alpha= 0.6;

%% first order differential equation %%

dcdt(1) = -K_2*c(1);                        % Rubber
dcdt(2) = K_2*c(1)-K_3*c(2)-K_4*c(2);       %Ia
dcdt(3) = K_4*c(2)-K_5*c(3);                %Ib
dcdt(4) =  K_3*c(2)+ K_5*c(3);              %v+c

end
```

A-2 MATLAB code for Determination of heat transfer across the reactor zones

```
numberOfPDE = 1;
pdem = createpde(numberOfPDE);
r1 = [3 4 0 0 0.2 0.2 0 0.3 0.3 0 ];
r2 = [3 4 0 0 0.2 0.2 0.3 1.7 1.7 0.3 ];
r3 = [3 4 0 0 0.2 0.2 1.7 2 2 1.7 ];
gdm = [r1; r2; r3]';
g = decsg(gdm,'R1+R2+R3',['R1'; 'R2'; 'R3']');
geometryFromEdges(pdem,g);
figure
pdegplot(pdem,'EdgeLabels','on');
axis([-0.1 2.1 -0.1 0.5]);
title 'reactor Geometry With Edge Labels Displayed'
hmax = .05; % element size
msh=generateMesh(pdem,'Hmax', hmax);
figure
pdeplot(pdem);
axis equal
title 'Block With Finite Element Mesh Displayed i.e= Dx=Dy'
%Boundary conditions:
T1 = applyBoundaryCondition(pdem,'Edge',[5],'g',193285,'q',250); % 'Edge' Forced convection
%moderate speed cross flow of air- 200 w/m^2 K
T2 = applyBoundaryCondition(pdem,'Edge',[1,2,3,4,6,7,8,9,10],'g',7378.75,'q',25); % 'Edge' free convection 5 w/m^2 K
%for 2-D
%%thermophysical property of sheet metal
rho = 7870; % density of iron 7870 kg/m^3
Cp = 1.625; % specific heat 1.625J/kg K
k = 54; % thermal conductivity of carbon steel max 0.5% C W/m K
%%
c = k;
a = 0;
f = 0;
d = rho*Cp;
u = assempde(pdem, c, a, f);
figure
pdeplot(pdem, 'xydata', u, 'contour', 'on', 'colormap', 'jet');
axis equal
title 'Temperature, Steady State Solution before the introd. of tire; Temp in [K]'

p=msh.Nodes;
plotAlongY(p, u, 0);
title 'Temperature variation with reactor length'
xlabel 'X-coordinate, meters'
ylabel 'Temperature, degrees-Kelvin'
```

A-3: Detail screw conveyor Component Design

Since, the tire particle have to get enough activation energy/heat energy to fully decompose to the required by products, the residence time plays a great role on the conveyor velocity.

Therefore, axial velocity *v* is given as

V = reactor length/residence time [m/sec] *(A-3.1)*

Reactor length: 2m

Residence time: 15-30 min, taking the average: 22.5 min (1,350 sec)

V = 2m/1350 sec = 1.48×10^{-3} *m/s, 0.089 m/min*

From [44], the speed of conveyer relation with the rotational frequency/revolutions per minutes is given as

$$V = \frac{tn}{60} \qquad \text{(A-3.2)}$$

Where t = pitch of the screw (lead) [m], t=d because of selection of full pitch (diameter of screw)

n = rpm of the screw

$$n = 60 * \frac{v}{t}$$

$$n = (60 * 0.089\, m/min)/(0.19m)$$

$$n = 28\, rpm$$

In actual case, the screw speed is between 10-30 rpm. This phenomena also accompanied by [48], a large screw conveyor diameter is required for lower screw conveyor speeds.

The required capacity of the pyrolysis plant is to process 15 kg of waste tires within an hour and the recommended trough loading percentage is planned to occupy 30% of the trough is solid state to allow the produced gases/volatiles to occupy the 70% of the trough.

In addition, [44] states that “the screw diameter D is governed by the lump size, being at last 12 times that of uniform lump size and at least four times the maximum lump size in case of un-sized bulk materials. Therefore, with a particle size ranging from 5mm to 15mm (max), the screw diameter at max lump size is closest to 180-190mm diameter.

The hourly capacity of screw conveyor can be calculated as [44]

$$Q = 3600\varphi \frac{\pi D^2}{4} \gamma \frac{tn}{60} k \tag{A-3.3}$$

Where: *Q is Hourly capacity in Kg/hr,*

φ is capacity factor (for heavy-weight abrasive loads- 0.125) [44]

D is the screw diameter same as the pitch (t)_standard full pitch screw

γ is the specific weight of the material (1,100 kg/m^3) [30]

n is the rpm of the screw, take 10 rpm

K is inclination factor (since the screw is horizontal one with zero degrees, k=1)

Therefore, ***Q becomes = 444 kg/hr***

The power requirement to drive a horizontal screw conveyor can be calculated as [44]

$$Nh = Co \frac{QL}{367} \tag{A-3.4}$$

Where N_h *= power requirement for horizontal conveyor*

Co = Friction factor (for pulverized coals and ground chalk-the value is given as 1.6)

L = Conveyor length [m] – 2 meters

Q = hourly capacity in tons/h – 0.444 tons/hr

Therefore, N_h *becomes =* $3.87x10^{-3}$ *KW*

With a mechanical transmission efficiency of η = 0.75, the required motor power will be

No = Nh/ η= $3.87x10^{-3}$ *KW / 0.75 =* $5.1x10^{3}$ *KW*

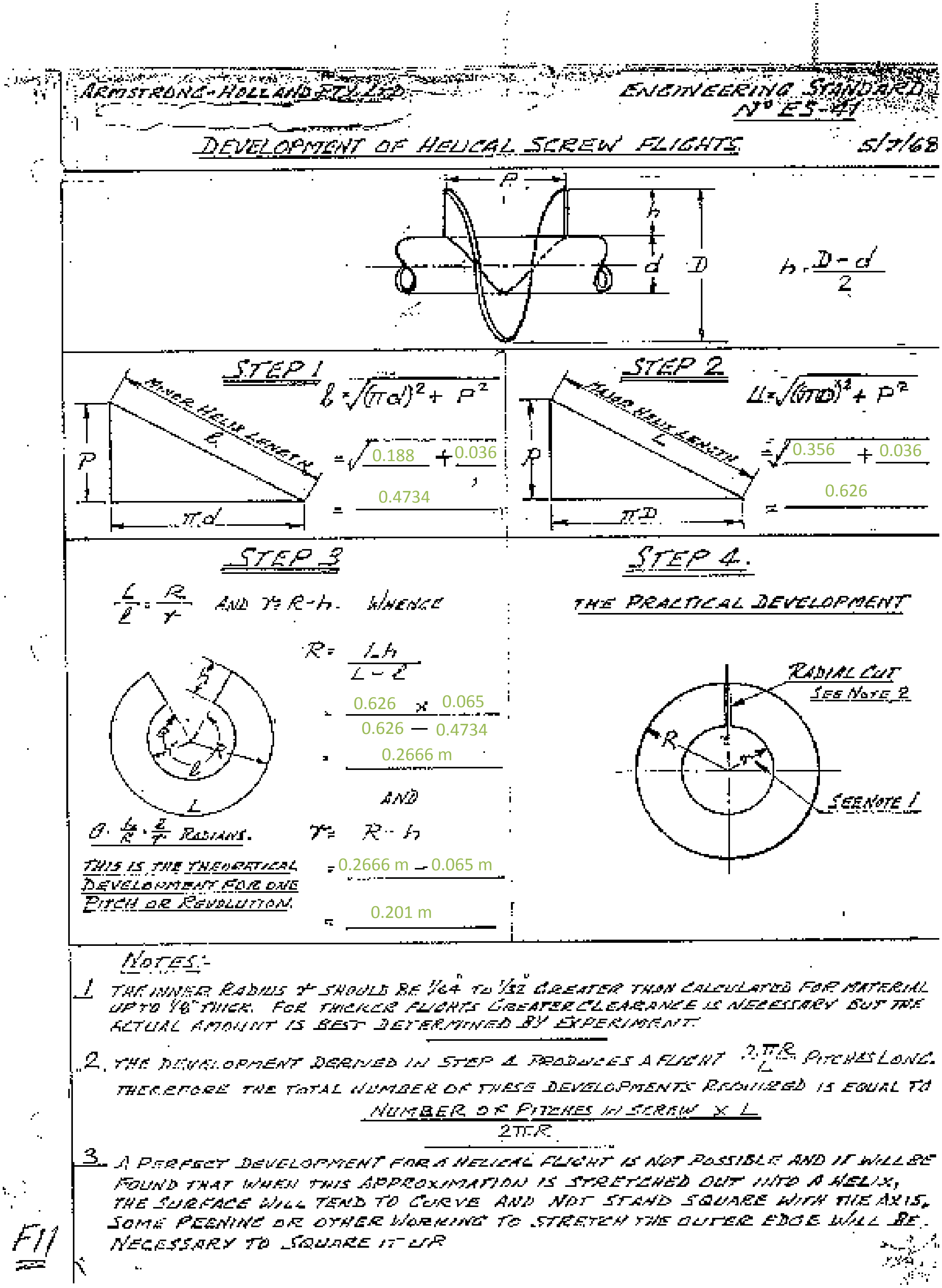
Motor selection: available motor sizes are 1.5 KW and above for industrial applications.

Internal diameter for 60 mm were used for light shaft loads and ease of screw flights manufacturing and weldment. In order to find the internal diameter, a development of helical screw flights are required prior to the engagement of production.

Therefore, the practical development of screw flights are

R = 266.6 mm and r = 201 mm

The screw flight were manufactured with this regard.



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ENGINEERING STANDARD
Nº ES-41

DEVELOPMENT OF HELICAL SCREW FLIGHTS

5/7/68

$h = \frac{D-d}{2}$

STEP 1

$l = \sqrt{(\pi d)^2 + P^2}$

$= \sqrt{0.188 + 0.036}$

$= 0.4734$

STEP 2

$L = \sqrt{(\pi D)^2 + P^2}$

$= \sqrt{0.356 + 0.036}$

$= 0.626$

STEP 3

$\frac{L}{l} = \frac{R}{r}$ AND $r = R - h$. WHENCE

$R = \frac{Lh}{L - l}$

$= \frac{0.626 \times 0.065}{0.626 - 0.4734}$

$= 0.2666$ m

AND

$r = R - h$

$= 0.2666$ m $-$ 0.065 m

$= 0.201$ m

$\theta = \frac{L}{R} = \frac{l}{r}$ RADIANS.

THIS IS THE THEORETICAL DEVELOPMENT FOR ONE PITCH OR REVOLUTION.

STEP 4.

THE PRACTICAL DEVELOPMENT

NOTES:-

1. THE INNER RADIUS r SHOULD BE 1/64" TO 1/32" GREATER THAN CALCULATED FOR MATERIAL UP TO 1/8" THICK. FOR THICKER FLIGHTS GREATER CLEARANCE IS NECESSARY BUT THE ACTUAL AMOUNT IS BEST DETERMINED BY EXPERIMENT.

2. THE DEVELOPMENT DERIVED IN STEP 4 PRODUCES A FLIGHT $\frac{2\pi R}{L}$ PITCHES LONG. THEREFORE THE TOTAL NUMBER OF THESE DEVELOPMENTS REQUIRED IS EQUAL TO

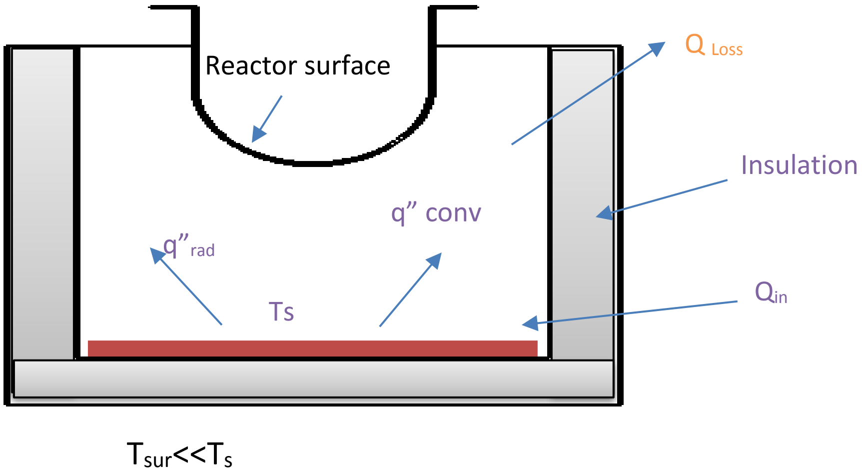
$$\frac{\text{NUMBER OF PITCHES IN SCREW} \times L}{2\pi R}$$

3. A PERFECT DEVELOPMENT FOR A HELICAL FLIGHT IS NOT POSSIBLE AND IT WILL BE FOUND THAT WHEN THIS APPROXIMATION IS STRETCHED OUT INTO A HELIX, THE SURFACE WILL TEND TO CURVE AND NOT STAND SQUARE WITH THE AXIS. SOME PEENING OR OTHER WORKING TO STRETCH THE OUTER EDGE WILL BE NECESSARY TO SQUARE IT UP.

F11

A-4: combined Heat transfer within the reactor

The heated bottom surface of the biomass furnace, a simultaneous heat transfer occurs by forced convection originated by the blower and radiation due to the heated surface.



The net heat transfer from the surface, expressed per unit area of the surface is given by [49]

$$q''rad = q/A = \varepsilon\sigma\,(Ts^4 - Tsur^4) \tag{A-4.1}$$

$$\text{Also, } q = hrA(T_s - T_{sur}) \tag{A-4.2}$$

$$\text{Where } hr = \varepsilon\sigma\,(Ts+Tsur)(Ts^4 + Tsur^4) \tag{A-4.3}$$

The convective heat transfer process also van be calculated as

$$q''con = q/A = h(Ts - T\infty) \tag{A-4.4}$$

Where $h = 250$ *w/m2.K (Forced-convective heat transfer coefficient)*

$\sigma = 5.67\text{x}10^{-8}\ W/m^2.K^4$ *(Stefan-boltzmann constant)*

$\varepsilon = 0.8$ *(Emissivity)*

$T\infty$ *or* $Tsur$ *= Ambient temp (295.15) &* $Ts = 823.15$ *kelvin (Average)*

Therefore, the total heat flux per unit area of surface becomes $q'' = \varepsilon\sigma\,(Ts^4 - Tsur^4) + h(Ts - T\infty)$ *(A-4.5)*

q" = 152.47 KW/m

On the experimental run, the maximum outside (surface temperature) recorded was 54°C, therefore the Qloss can be found as same procedure by use of equation (A-4.5) (heat flux per unit meter)

Where Ts = 54°C or 327.15 kelvins

h = 25 w/m^2.k (Free convection heat transfer)

Qloss = 975.14 w/m

A-5: collected Mass loss data, product yield and thermal efficiency calculation

	First run	Wt. %	second run	Wt. %	third run	Wt. %
Initial tire Mass	15		15		15	
Mass of char	9.6645	64.43%	8.97	59.80%	8.13	54.20%
Mass of Gas	5.334	35.56%	5.796	38.64%	6.51	43.40%
Mass of oil	0.0015	0.01%	0.234	1.56%	0.36	2.40%

The liquid-phase of pyrolysis products is usually named pyrolysis oil. It is a dark, cloudy, dense liquid with a rather strong odour. Post-pyrolytic oil is a very complex mixture of hydrocarbons consisting of saturated and unsaturated linear or cyclic hydrocarbons with 7-20 carbon atoms per particle, resinous substances and the entrainment of black particles Oil yields vary between 38 and 56 wt% and the heating value is about 40-43 MJ/kg [58].

The pyrolysis solid residue is char, which is also called pyrolytic carbon black. It is mesoporous material with an average heating value of 30 MJ/kg [58].

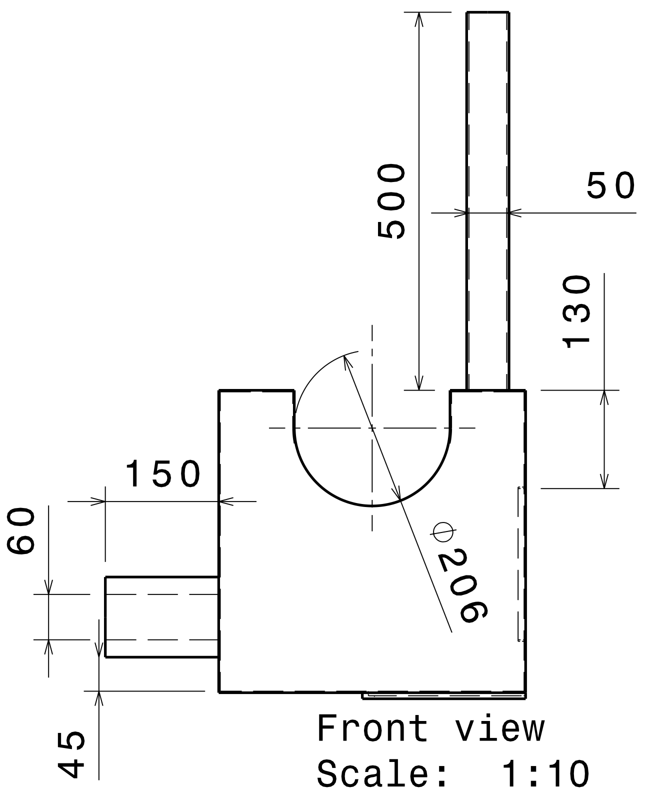
Gas obtained from the pyrolysis ofwaste tires is named pyrolytic gas, pyrogas or syngas. It can range from a few percent to more than ten percent of the products depending on the technology used and the process conditions. It has a high heating value, up to about 84 MJ/Nm^3 or 42 MJ/kg [58].

$$\eta char \quad = \frac{mchar\ x\ HHV\ char}{mtire\ x\ HHV\ tire} * 100 = \frac{\left(8.13\ kg\ x \frac{33.14 MJ}{kg}\right)}{15\ kg\ x\ 26\frac{MJ}{kg}} * 100 = 62.5\%$$

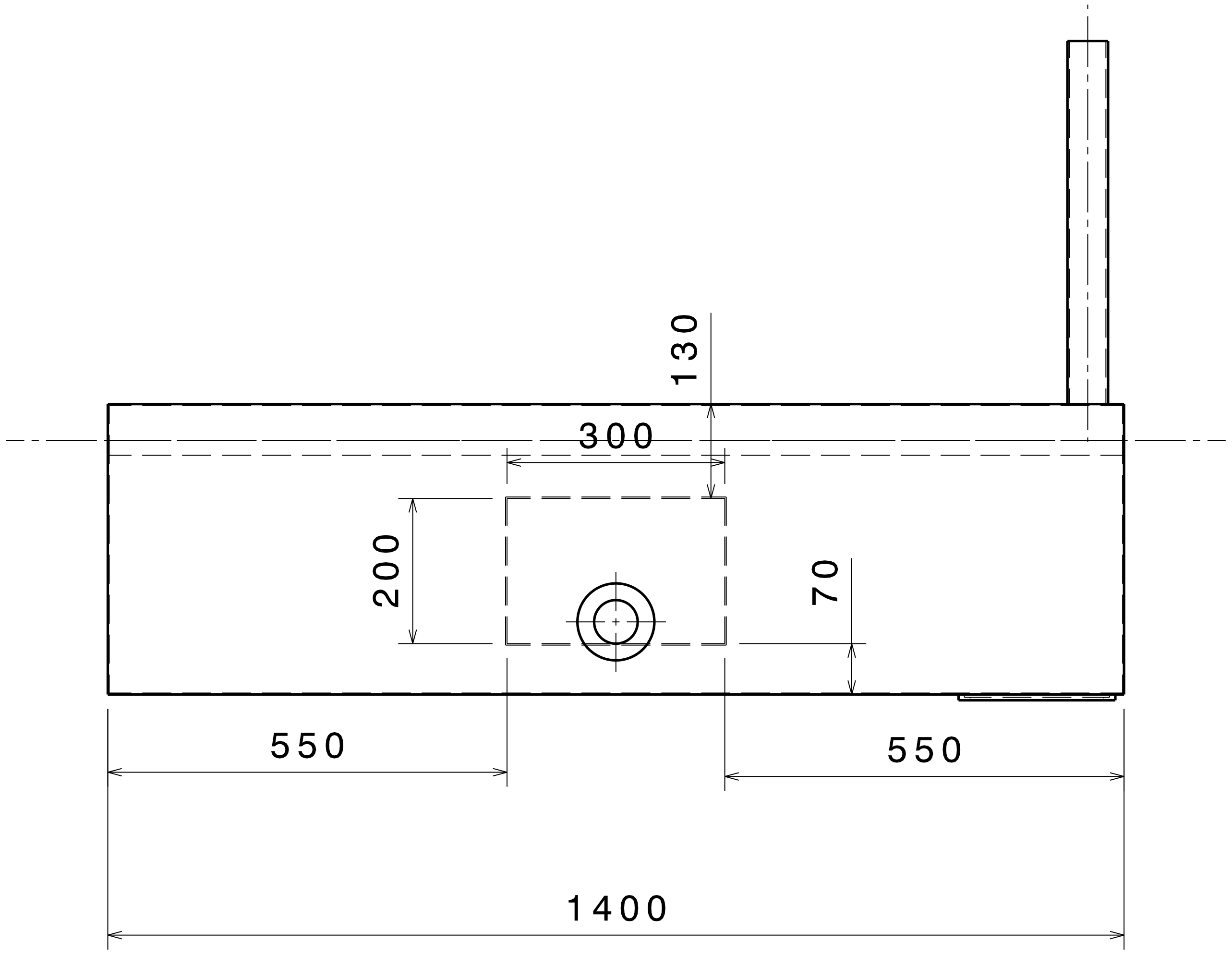
$$\eta pyro - oil \quad = \frac{mpyro{-}oil\ x\ HHV\ pyro{-}oil}{mtire\ x\ HHV\ tire} * 100 = \frac{0.36\ kg\ x\ 46.35\frac{MJ}{kg}}{15\ Kg\ x\ 26\frac{MJ}{kg}} * 100 = 3.69\%$$

$$\eta Gas \quad = \frac{mgas\ x\ HHV\ gas}{mtire\ x\ HHV\ tire} * 100 = \frac{6.51 Kg\ x\ 42\frac{MJ}{kg}}{15 Kg\ x\ 26\frac{MJ}{kg}} * 100 = 70.1\%$$

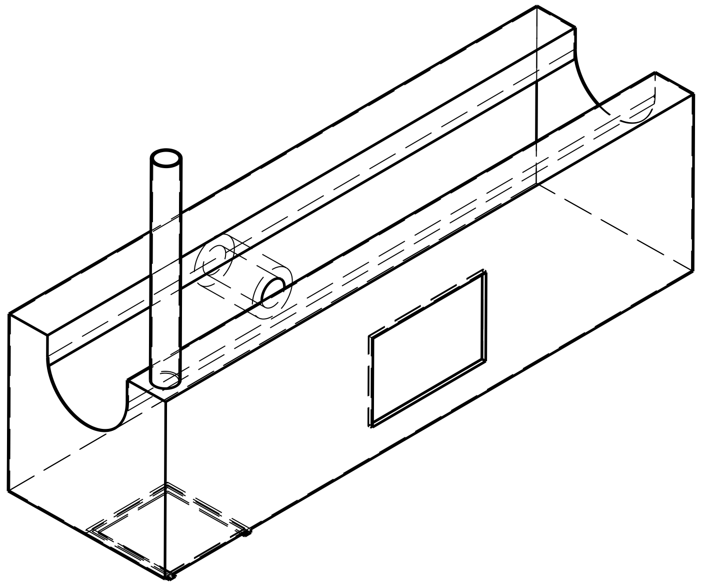
A-6: Detailed drawings of pyrolysis reactor



Front view
Scale: 1:10



Left view
Scale: 1:10



Isometric view
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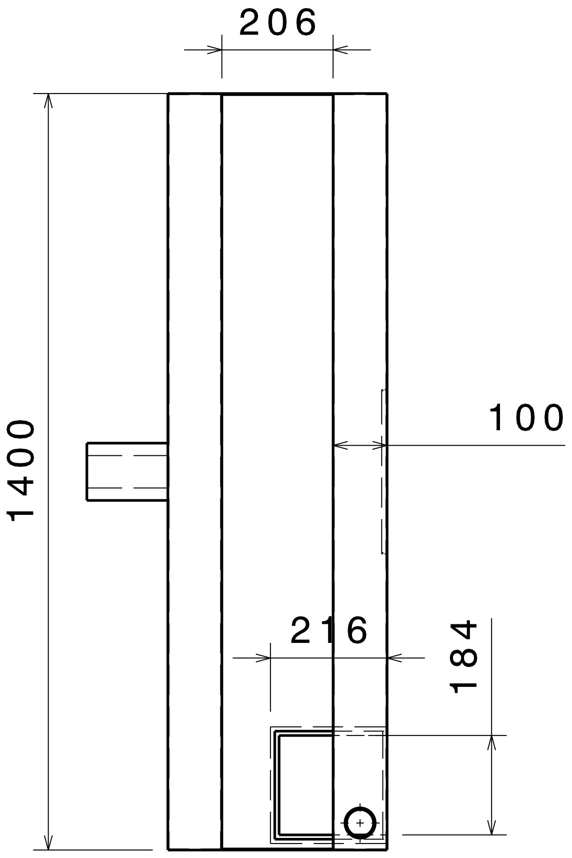

Top view
Scale: 1:14

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AAiT

DRAWING TITLE
Biomass furnance

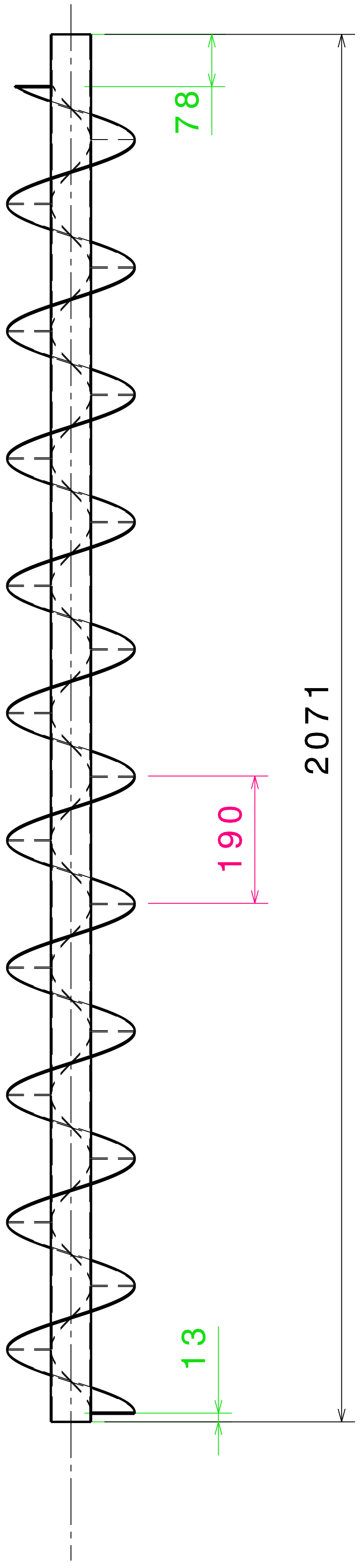
DRAWN BY
Yenealem
DATE
9/21/2018

CHECKED BY
Wondwosen
DATE
XXX

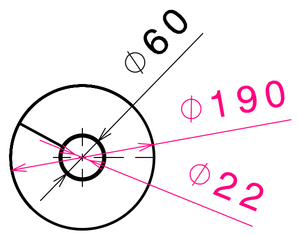
DESIGNED BY
XXX
DATE
XXX

SIZE
A3
DRAWING NUMBER
REV
X

SCALE 1:1
WEIGHT(kg) 46.19
SHEET 1/1



Front view
Scale: 1:10



Top view
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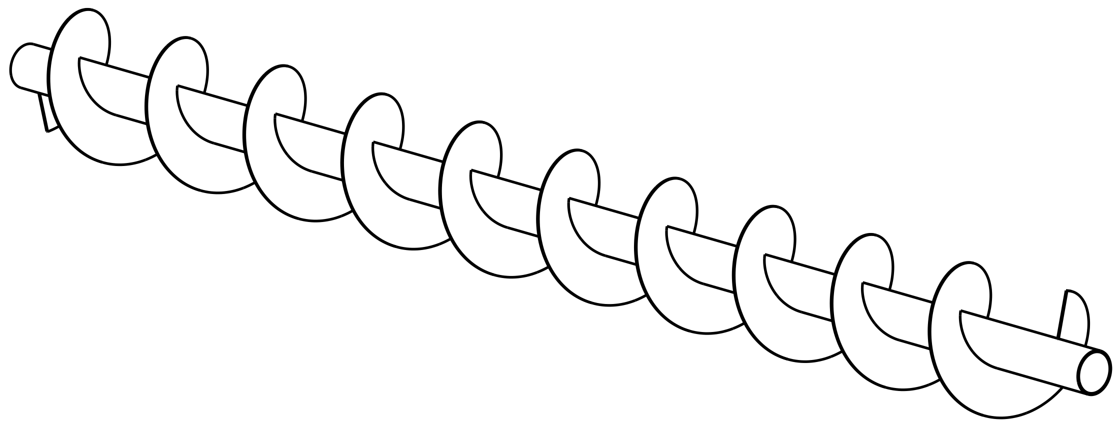

Isometric view
Scale: 1:10

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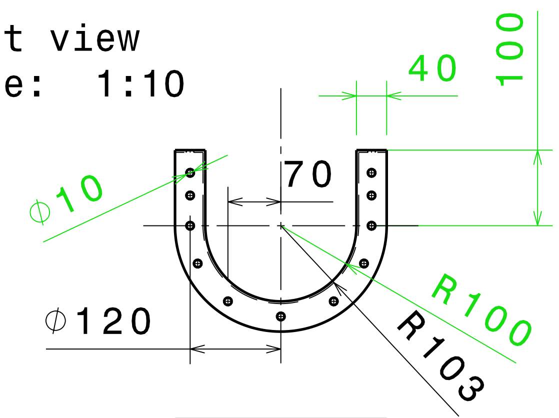
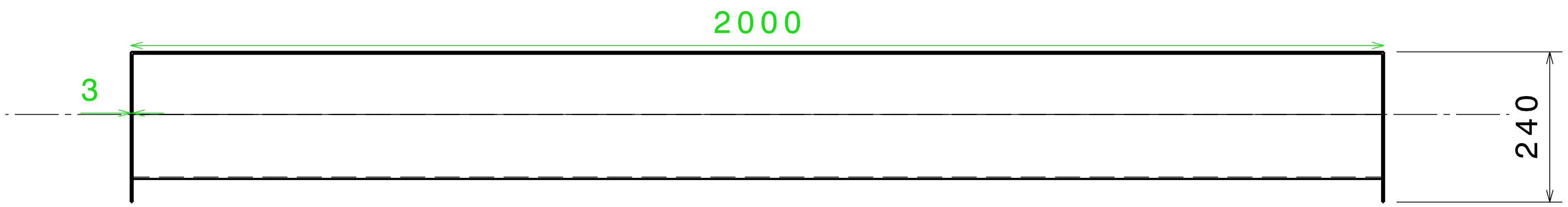
AAiT

DRAWN BY Yenealem	DATE 9/5/2018	DRAWING TITLE Screw conveyor	
CHECKED BY wondwossen	DATE XXX	SIZE A3	DRAWING NUMBER	REV X
DESIGNED BY XXX	DATE XXX	SCALE 1:10	WEIGHT(kg) 1.25	SHEET 1/1

Front view
Scale: 1:10





Left view
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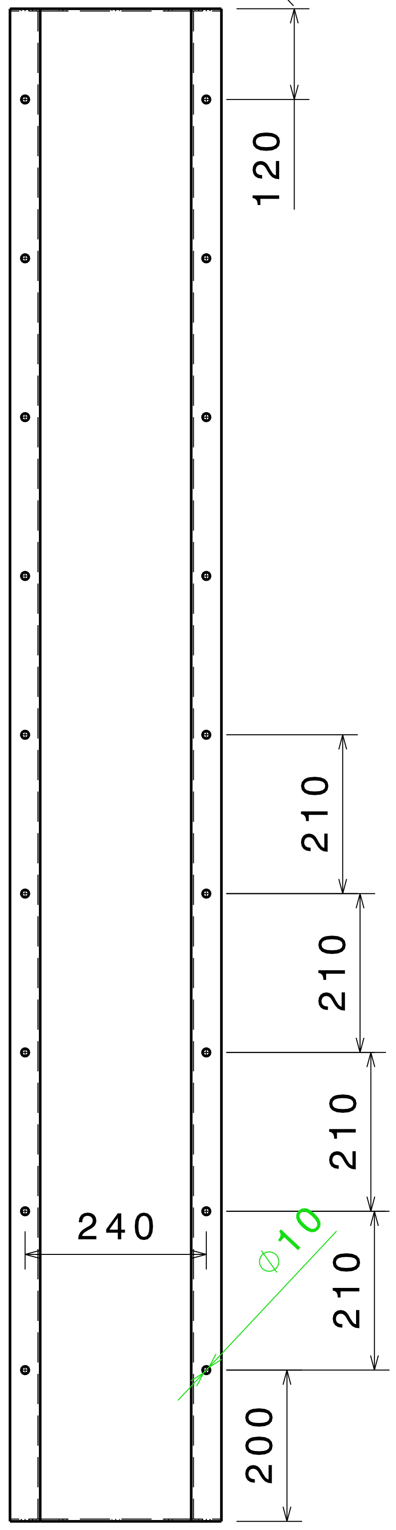

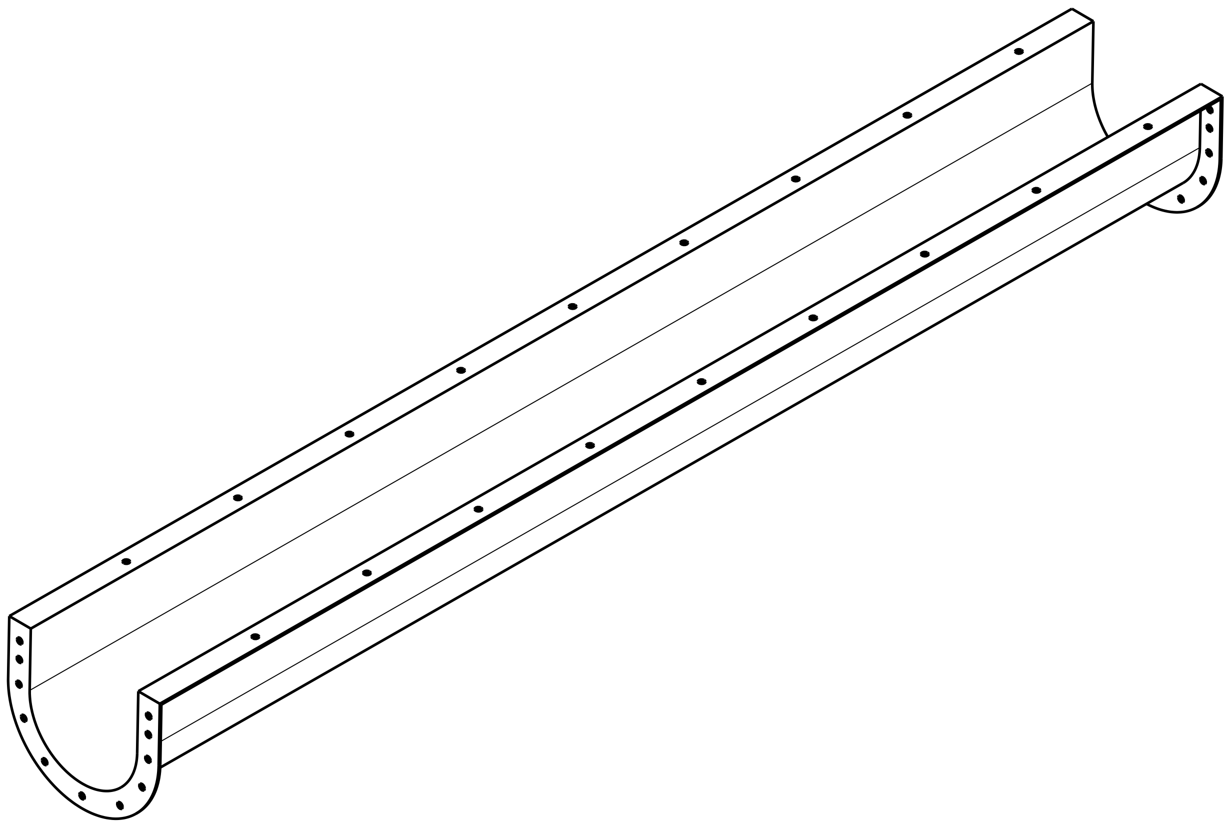

Isometric view
Scale: 1:10

Top view
Scale: 1:10

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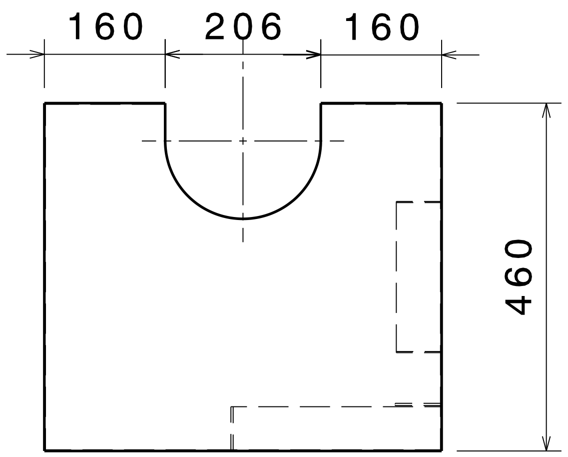
DRAWN BY Yenealem	DATE 9/5/2018	DRAWING TITLE Trough / Screw casing			
CHECKED BY wondwossen	DATE XXX	SIZE A3	DRAWING NUMBER		REV X
DESIGNED BY XXX	DATE XXX	SCALE 1:10	WEIGHT(kg) 28.89		SHEET 1/1



Front view
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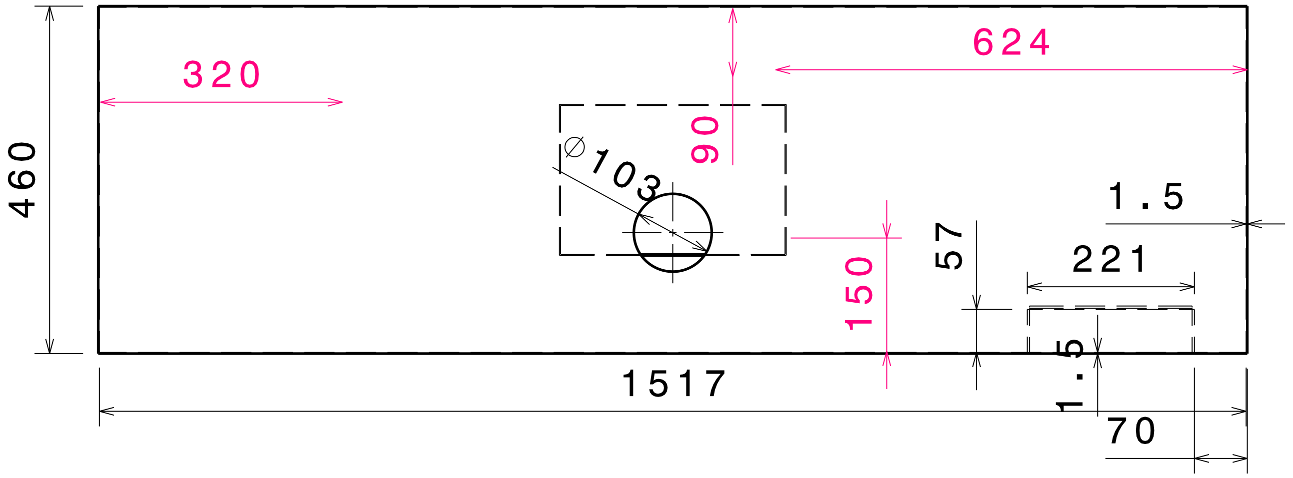
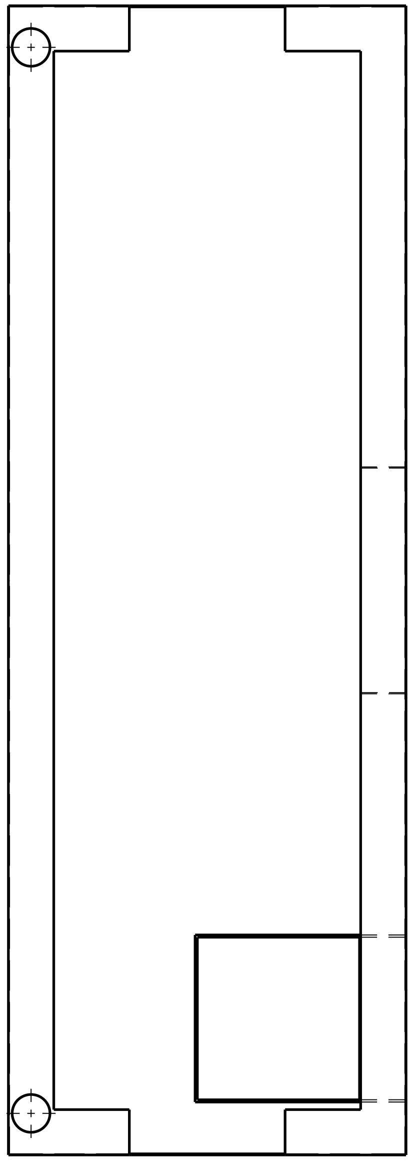
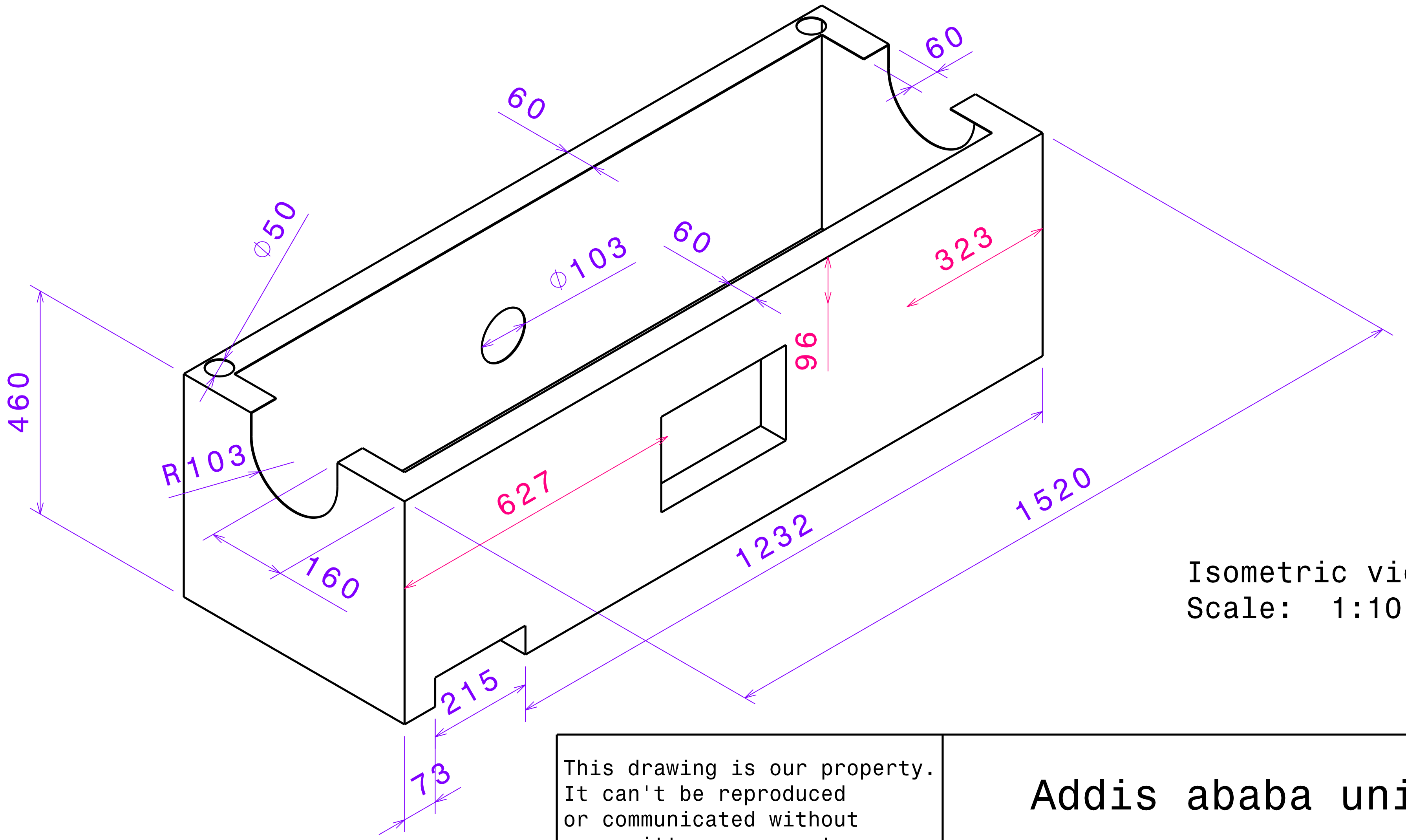


Left view
Scale: 1:10



Top view
Scale: 1:10



Isometric view
Scale: 1:10

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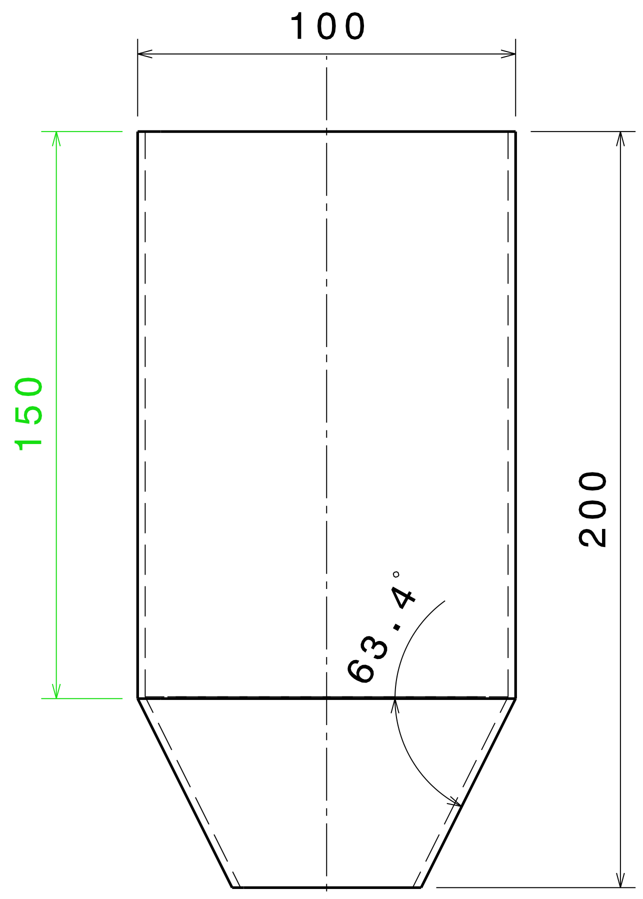
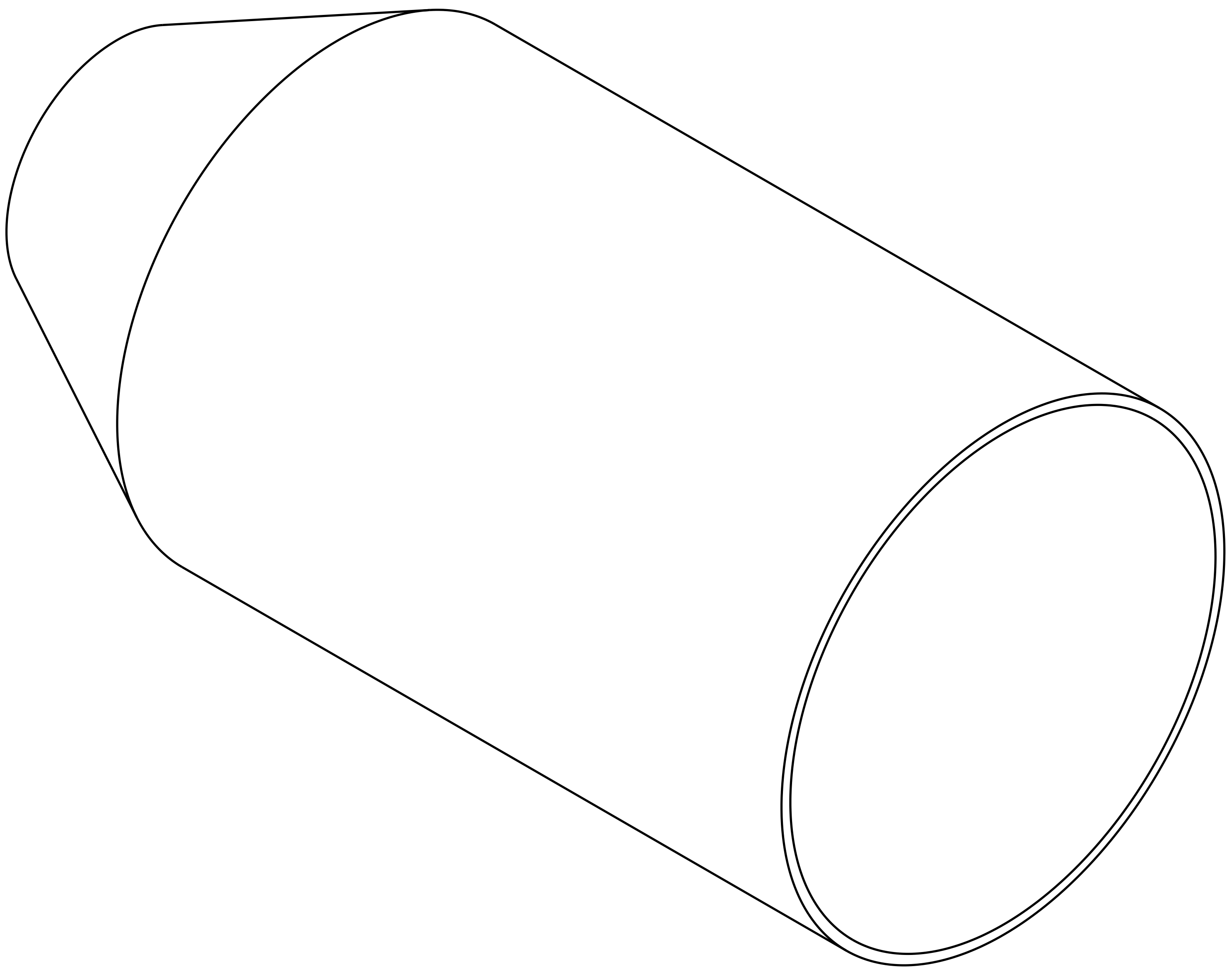
DRAWN BY Yenealem	DATE 9/5/2018	DRAWING TITLE Furnance enclosure	
CHECKED BY Wondwossen	DATE XXX	SIZE A3	DRAWING NUMBER
DESIGNED BY XXX	DATE XXX	SCALE 1:10	WEIGHT(kg) 64.81

REV X

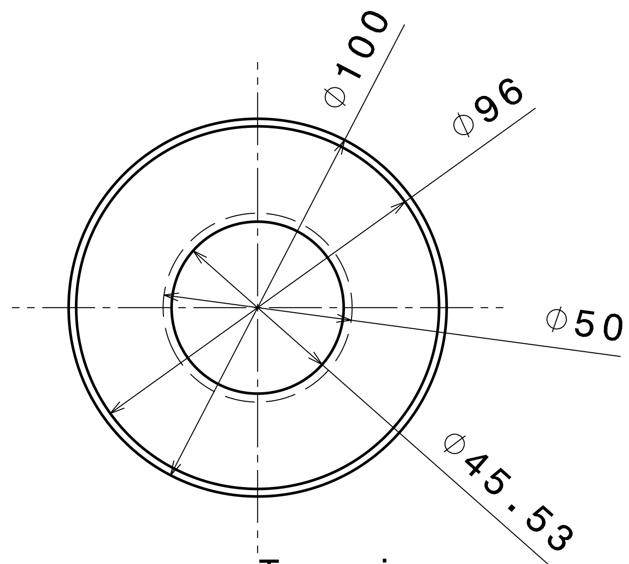
SHEET 1/1



Front view
Scale: 1:2



Isometric view
Scale: 1:1



Top view
Scale: 1:2

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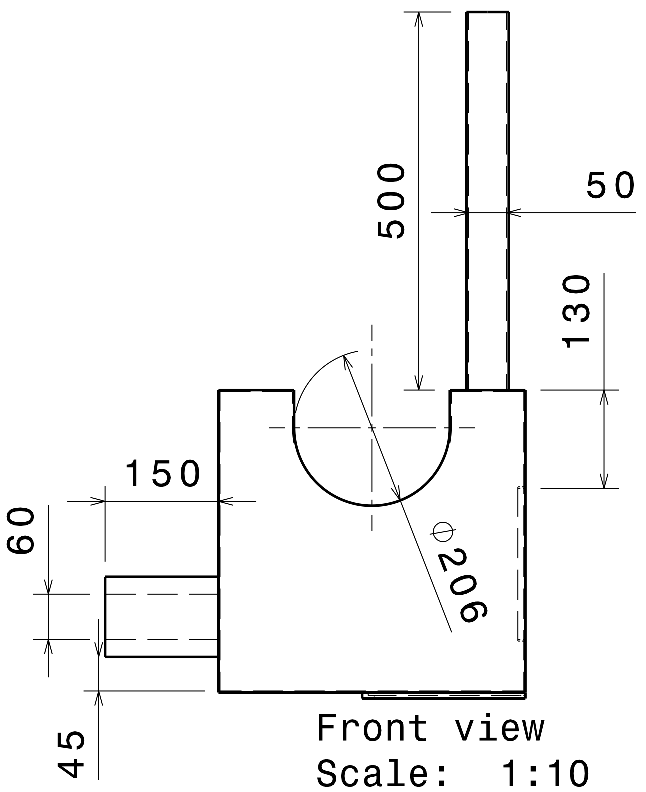
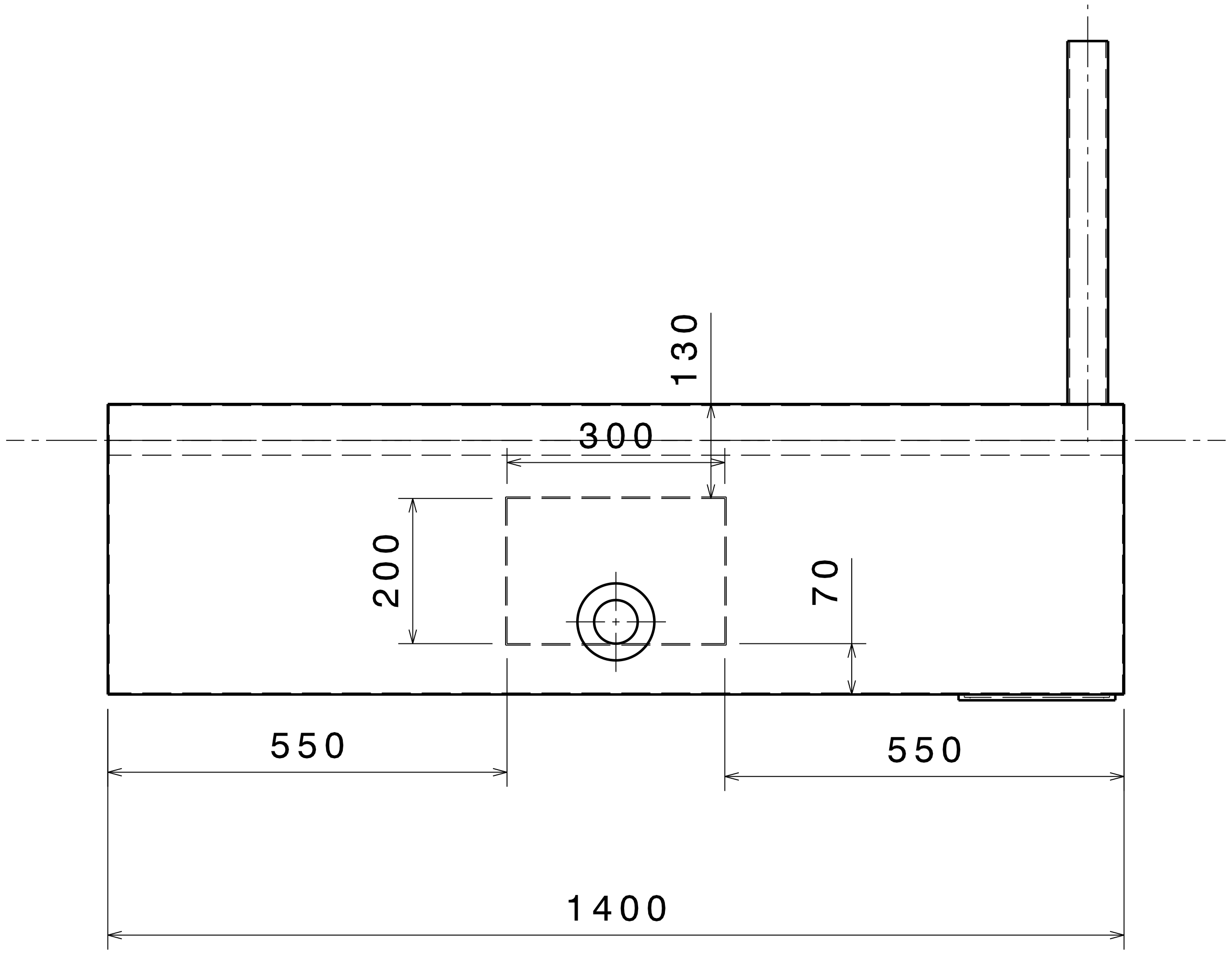
DRAWN BY Yenealem	DATE 9/5/2018	DRAWING TITLE Char Collector		
CHECKED BY wondwossen	DATE XXX	SIZE A3	DRAWING NUMBER	REV X
DESIGNED BY XXX	DATE XXX	SCALE 1:2	WEIGHT(kg) 0.93	SHEET 1/1



Front view
Scale: 1:10



Left view
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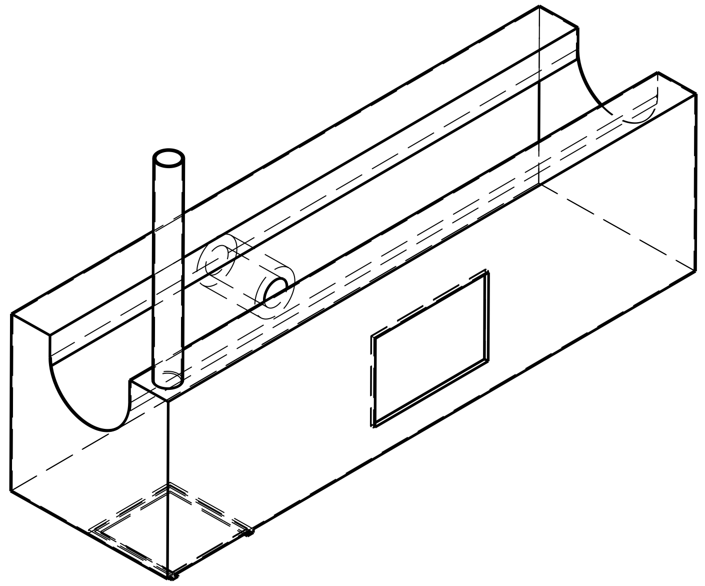
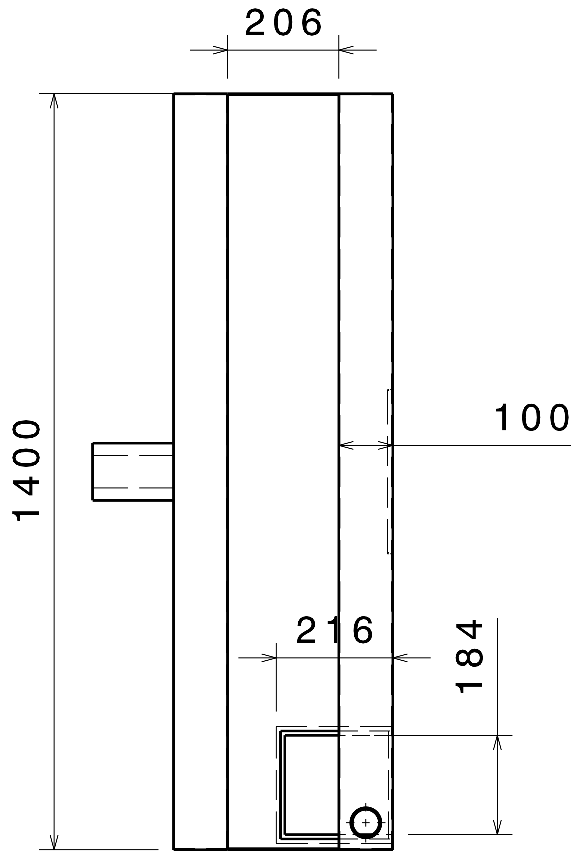


Isometric view
Scale: 1:14



Top view
Scale: 1:14

DASSAULT SYSTEMES

DRAWING TITLE

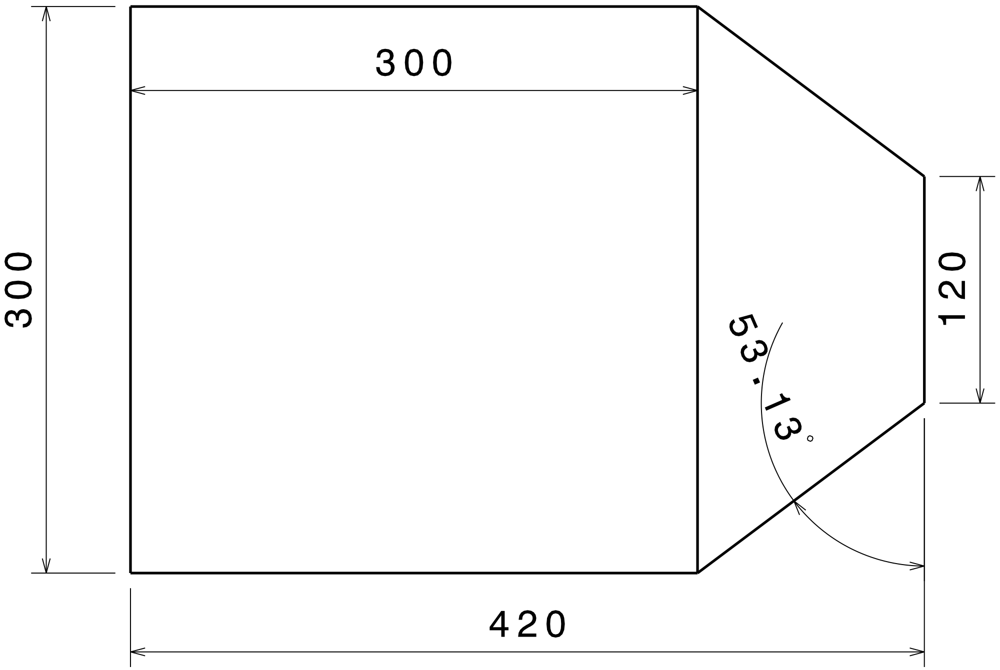
DRAWN BY
Yenealem
DATE
9/21/2018

CHECKED BY
Wondwosen
DATE
XXX

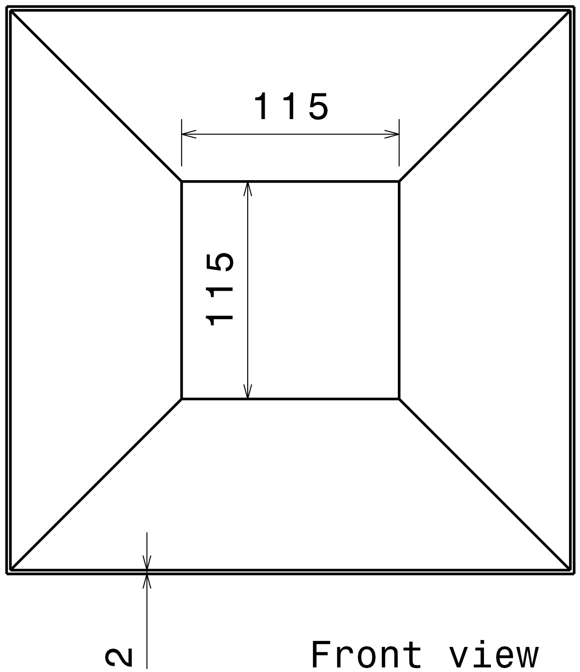
DESIGNED BY
XXX
DATE
XXX

SIZE
A3
DRAWING NUMBER
stand for reactor
REV
X

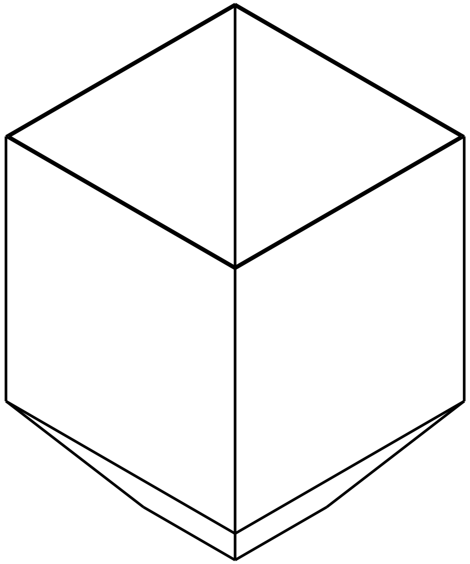
SCALE 1:1
WEIGHT(kg) 46.19
SHEET 1/1



Right view
Scale: 1:1



Front view
Scale:1:1



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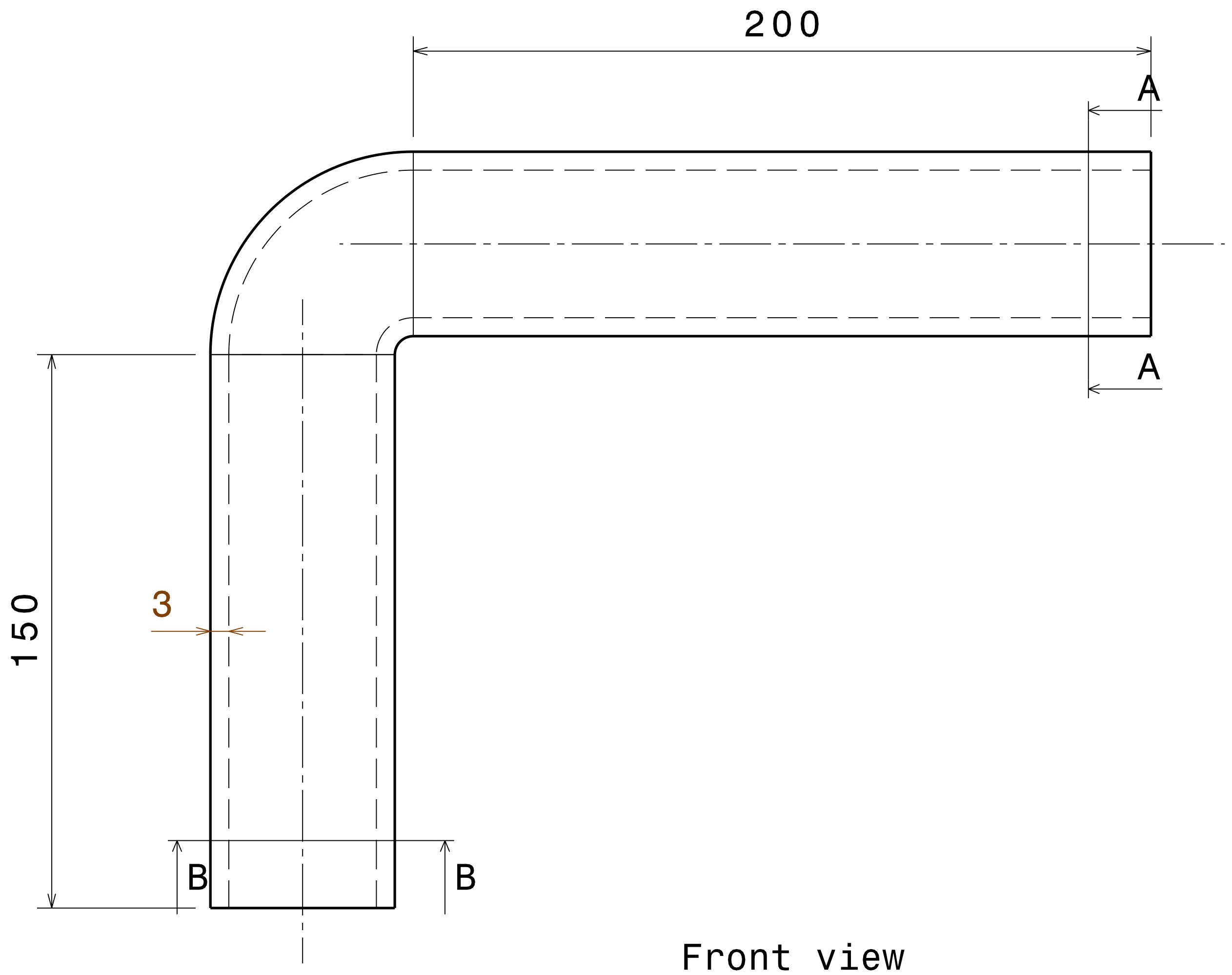
Feeding hopper

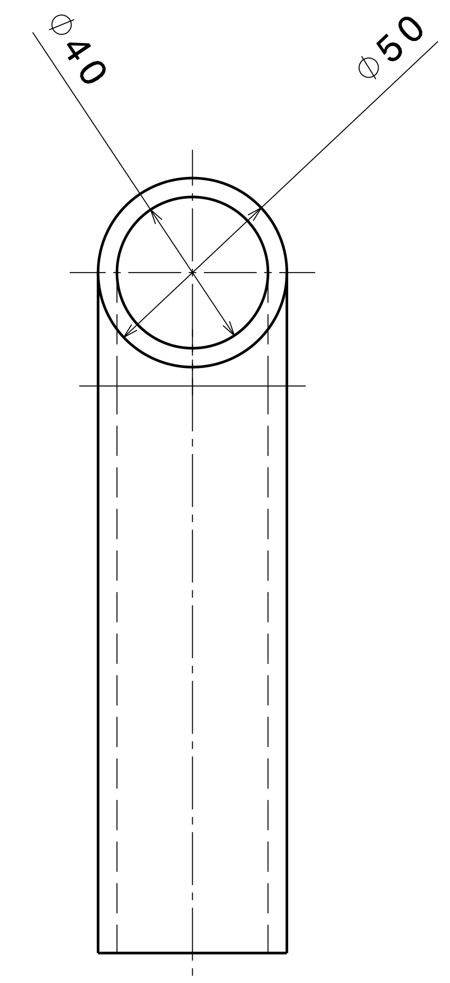
DRAWN BY Yenealem A.	DATE 7/11/2019	DRAWING TITLE	
CHECKED BY Dr. Wondwossen	DATE XXX	SIZE A4	DRAWING NUMBER Part2
DESIGNED BY XXX	DATE XXX	SCALE 1:1	WEIGHT(kg) 0.96

REV X

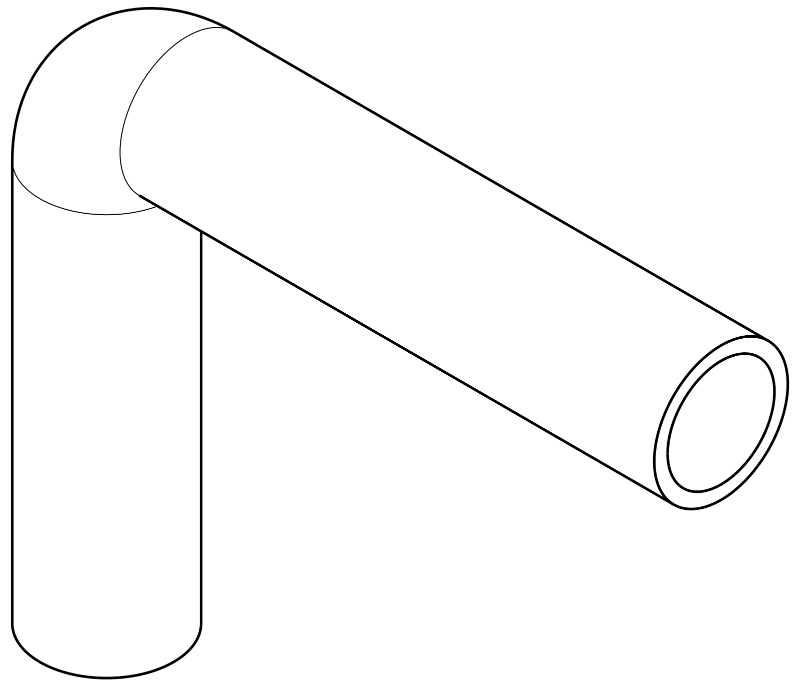
SHEET 1/1



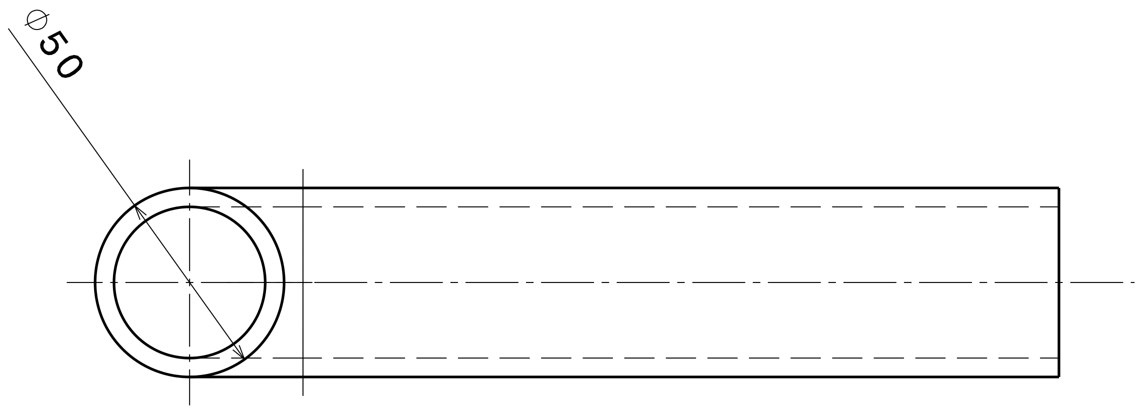
Front view
Scale: 1:2



Auxiliary view A
Scale: 1:2



Isometric view
Scale: 1:2



Auxiliary view B
Scale: 1:2

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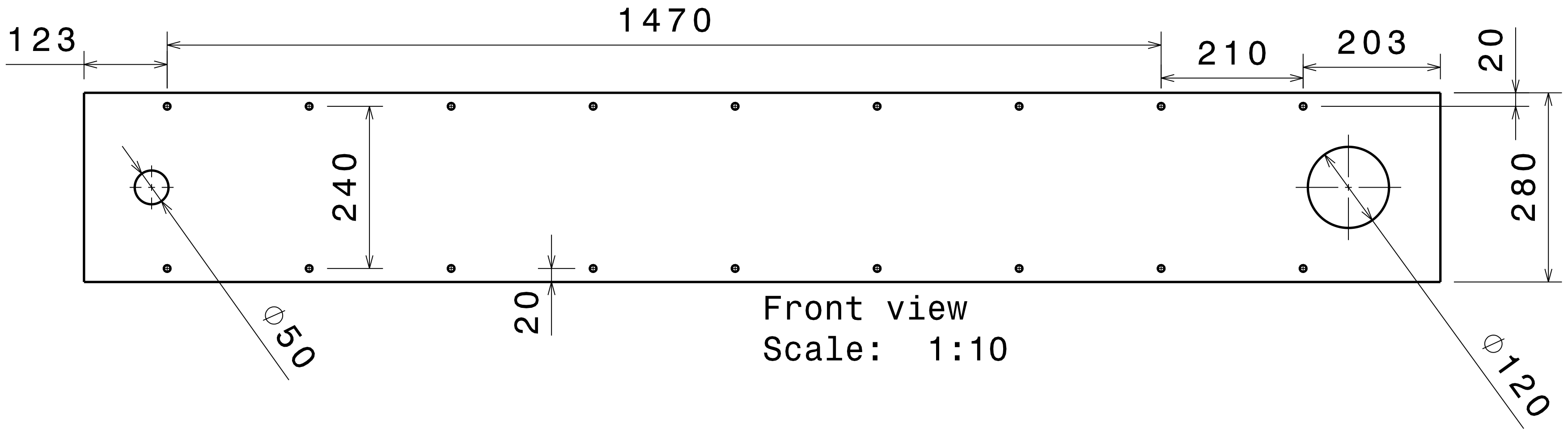
DRAWING TITLE
Gas outlet Pipe

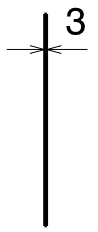
DRAWN BY Yenealem
DATE 9/5/2018
CHECKED BY Wondwossen
DATE XXX
DESIGNED BY XXX
DATE XXX

SIZE A3
DRAWING NUMBER
REV X

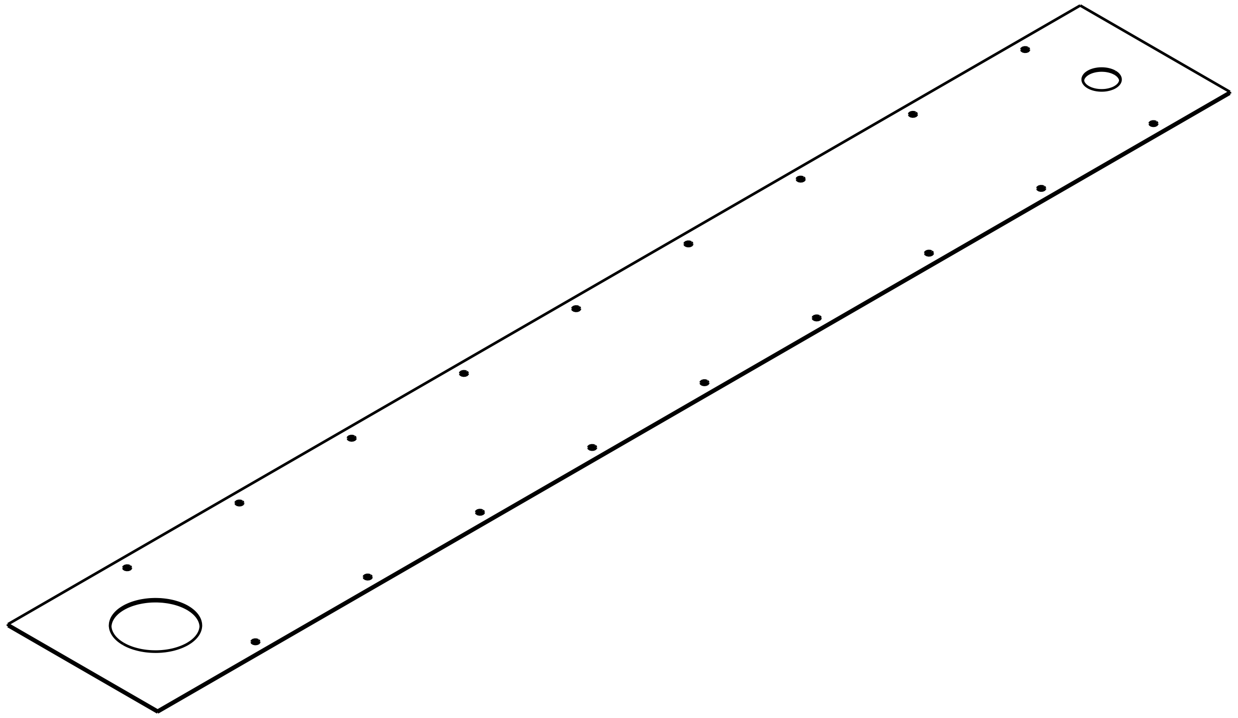
SCALE 1:2
WEIGHT(kg) 2.21
SHEET 1/1



Front view
Scale: 1:10



Left view
Scale: 1:10



Isometric view
Scale: 1:10

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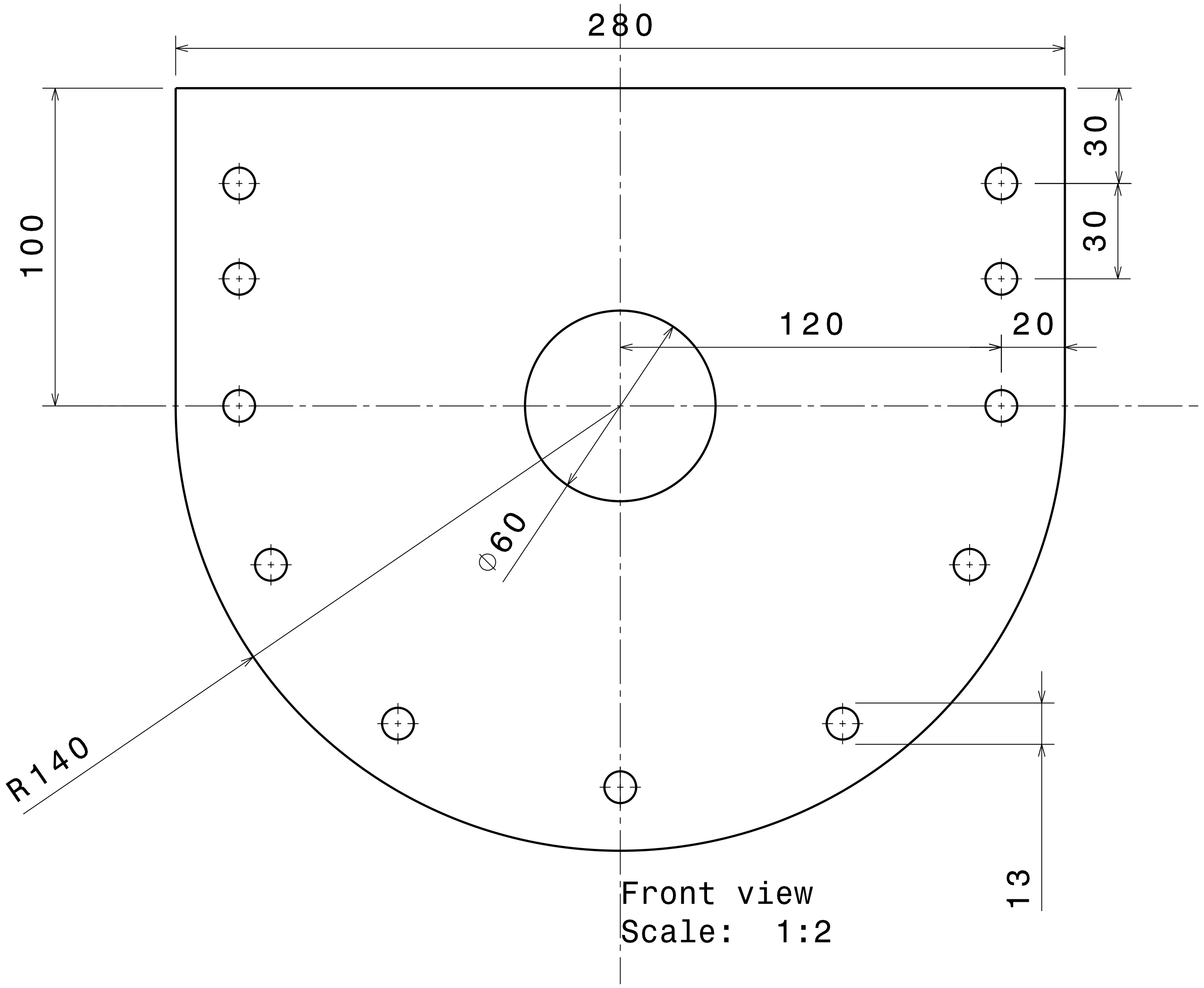
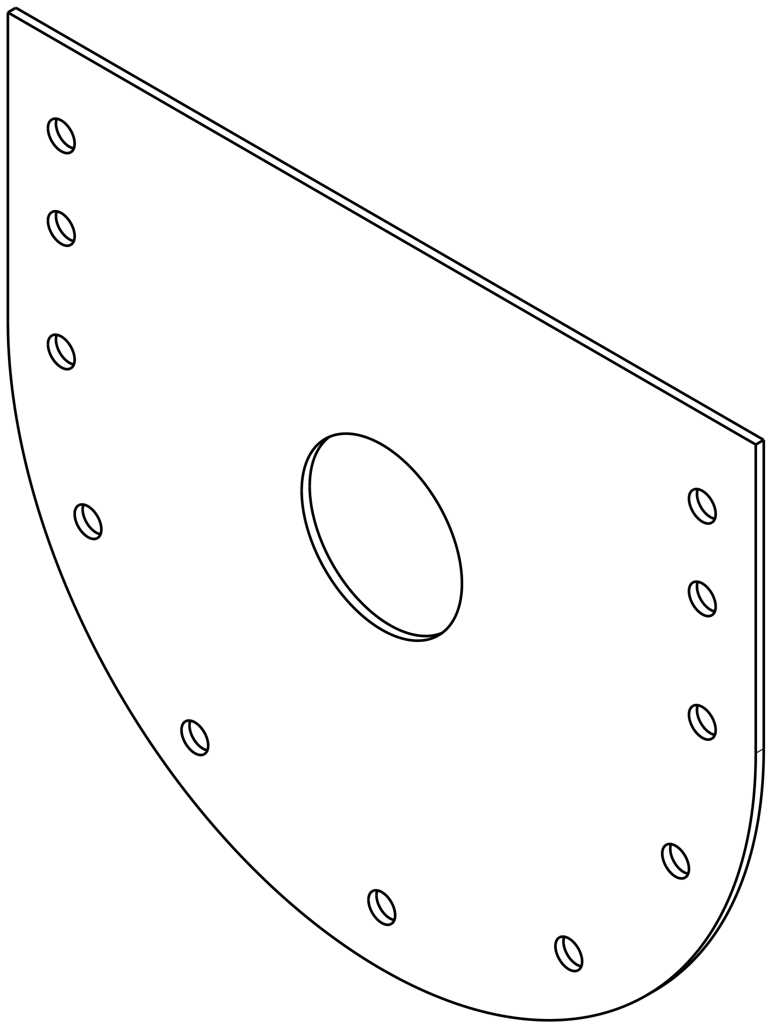
DRAWING TITLE
Screw Case top cover

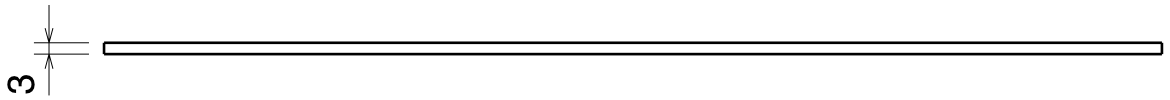
DRAWN BY Yenealem	DATE 9/5/2018	SIZE A3	DRAWING NUMBER		REV X
CHECKED BY Wondwossen	DATE XXX	SCALE 1:10	WEIGHT(kg) 12.90		SHEET 1/1
DESIGNED BY XXX	DATE XXX				



Front view
Scale: 1:2



Isometric view
Scale: 1:2



Top view
Scale: 1:2

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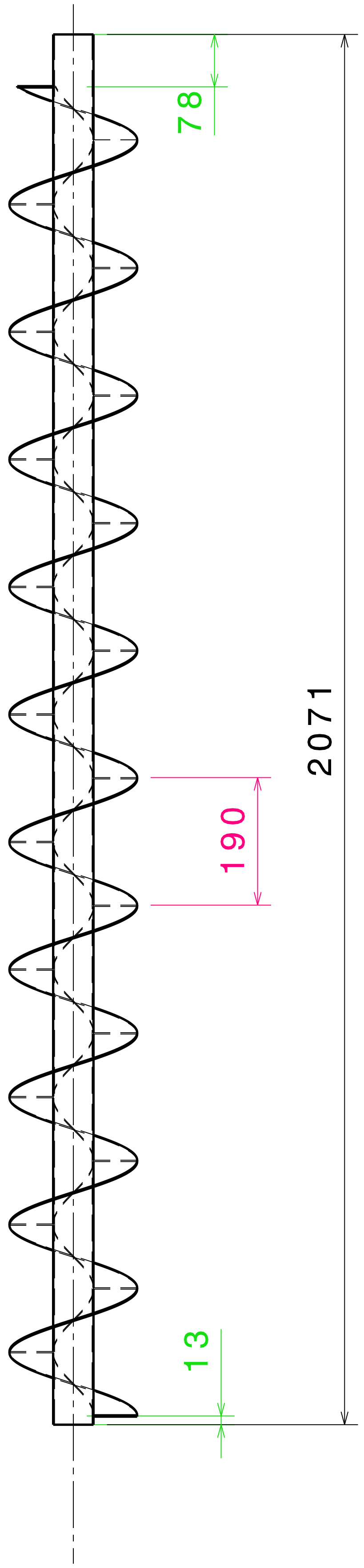
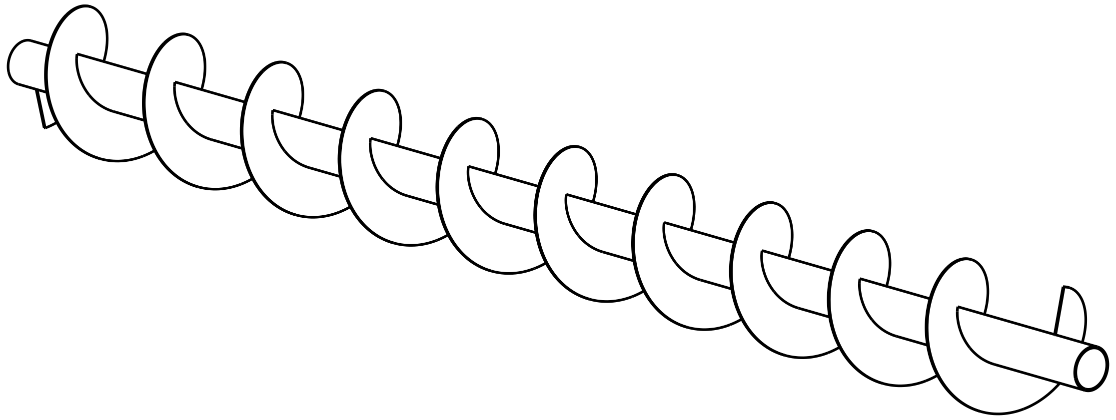
DRAWN BY Yenealem	DATE 9/5/2018	DRAWING TITLE	Screw Cover Plate
CHECKED BY Wondwossen	DATE XXX	SIZE A3	DRAWING NUMBER
DESIGNED BY XXX	DATE XXX	SCALE 1:2	WEIGHT(kg) 1.35

QTY 02

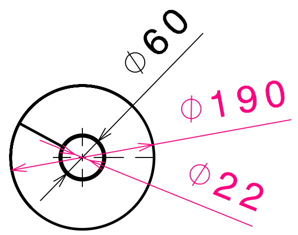
SHEET 1/1



Front view
Scale: 1:10



Isometric view
Scale: 1:10



Top view
Scale: 1:10

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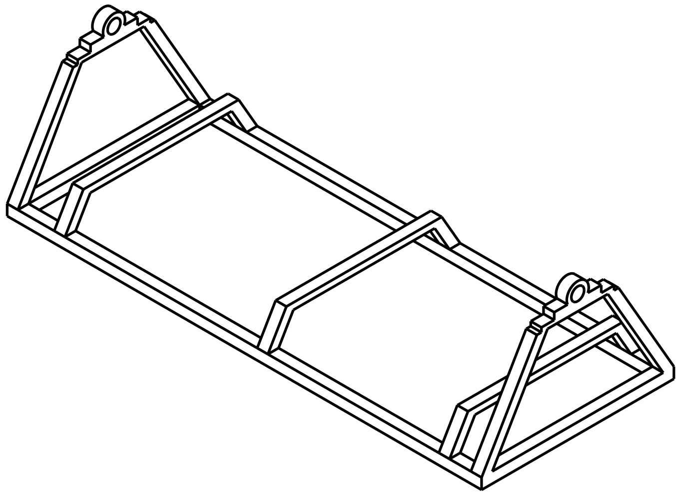
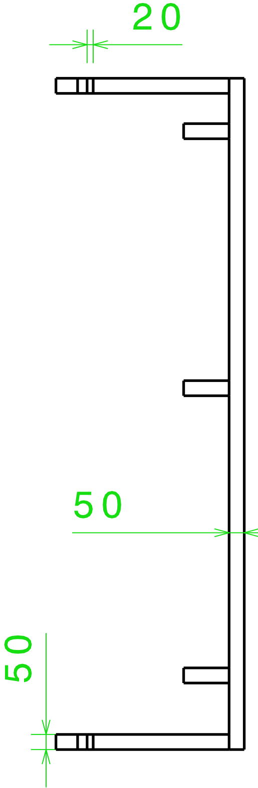
DRAWN BY Yenealem	DATE 9/5/2018	DRAWING TITLE	Screw conveyor
CHECKED BY wondwossen	DATE XXX	SIZE A3	DRAWING NUMBER
DESIGNED BY XXX	DATE XXX	SCALE 1:10	WEIGHT(kg) 1.25

REV X

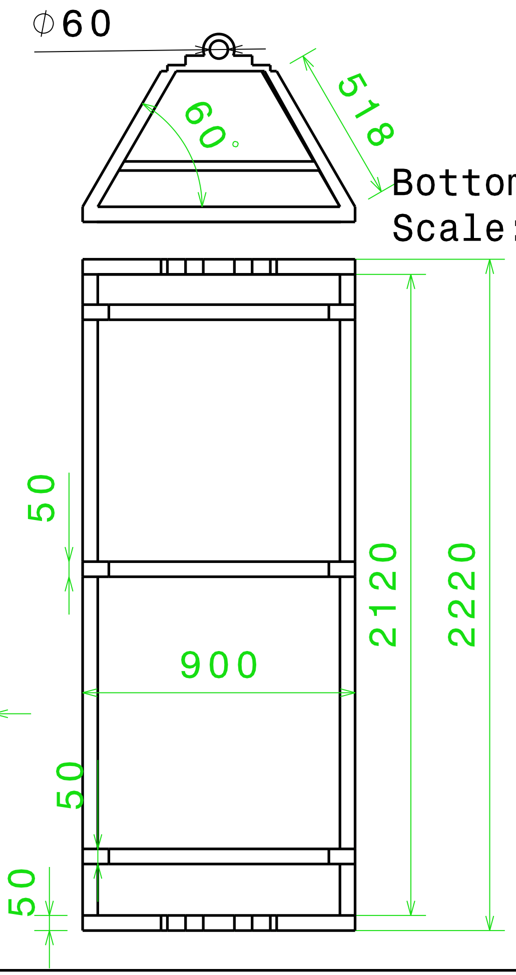
SHEET 1/1



Isometric view
Scale: 1:25



Right view
Scale: 1:1



Bottom view
Scale: 1:1

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AAiT

DRAWING TITLE
Support structure

DRAWN BY
Yenealem

DATE
7/11/2019

CHECKED BY
XXX

DATE
XXX

DESIGNED BY
XXX

DATE
XXX

SIZE
A4

DRAWING NUMBER

REV
X

SCALE 1:1

WEIGHT(kg) 0.00

SHEET 1/1