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EXPERIMENTAL INVESTIGATION OF FAST PYROLYSIS OF ARUNDO DONAX
IN A NOVEL PADDLE REACTOR

By

Chintan Kaushik Desai

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Mechanical Engineering

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2016

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE in Mechanical Engineering.

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Abstract

The main objective of this research was to show the effectiveness of a novel paddle reactor for fast pyrolysis and study the effect of biomass particle size and reaction temperature of Arundo Donax a type of energy crop on the bio-oil yields. The novel paddle reactor showed effective mixing and heat transfer which were proved with the help of studying the residence time and the heating characteristics of the system respectively. The effect of different biomass particle sizes on the bio-oil yield was not significant, the bio-oil yield was approximately 50% for all the sizes. For Arundo Donax particle sizes less than 1.0 mm would not have any significant effect on the bio-oil yield. The effect of reaction temperature on the bio-oil yield was not significant as the reaction temperature was increased from 500 to 530°C, the bio-oil yield decreased by 7% within that temperature range. Maximum bio-oil yield was obtained in the range of 470-500°C which was approximately 50%. A parabolic curve was obtained for reaction temperature vs bio-oil yield as predicted. For Arundo Donax the temperature for maximum bio-oil yield is about the same as for woody biomass, around 500°C.

CHAPTER 1. Introduction

Energy conversion is one of the most important areas in the field of science and technology. Improving the energy conversion processes and getting higher efficiency is one of the implicit task associated with any research. The common example of energy conversion is of IC engine in which the chemical energy of the fuel is converted into mechanical energy. All power producing machines need input source to generate power. Solar energy is the input source for solar cells, wind is for wind turbines and transportation fuels for automobiles.

In recent times due to a quasi-global focus on climate change, energy sources are mainly divided into two types: renewable and non-renewable (fossil). An EIA study suggests that by 2040 fossil fuels will supply the 80% of the energy demands and rest by renewable energy sources [1]. Looking at the energy demand and its consumption it is imperative to divert from current fossil fuel energy sources to renewable sources of energy so that we can have continuous energy supply [1]. In recent times, biomass which is available in abundance can be considered as a potential source for liquid fuels production, chemicals and other by products [2].

The main advantages of renewable sources are that they contribute little to no global warming potential, improved public health and environmental quality, provide support to energy supply, and if practiced sustainably can provide an inexhaustible and resilient supply of energy.

Biomass is recognized as a viable renewable source of energy which comprises of materials such as agriculture and forest residues, energy crops, municipal solid waste and algae are used to produce biofuels, chemicals and other byproducts such as char, synthetic gas (syn gas) and many more. Fast pyrolysis is one of the energy conversion process that has a potential to efficiently convert biomass to biofuels. Exploring one of these methods, the auger reactor technology is selected for detailed study in this thesis. The reason for selecting auger technology is due to its simple construction and working, no use of carrier gas and high bio-oil yields.

1.1. Background

The avid interest developed in the renewable field is because of the new policies and legislation such as US Energy Policy Act (EPA 2005) and Energy Independence and Security Act (EISA 2007) which mandates certain targets for biofuels. EIA projects that the world energy consumption will grow by 56% between 2010 and 2040, from 524 quadrillion British thermal units (Btu) to 820 quadrillion Btu. Renewable energy and nuclear power are the world's fastest-growing energy sources, each increasing 2.5% per year. However, fossil fuels continue to supply nearly 78% of world energy use through 2040. Natural gas is the fastest-growing fossil fuel, as global supplies of tight gas, shale gas, and coalbed methane increase [1]. But with this ever growing demand there is a strong need for renewable sources of energy so as to support the current energy supply.

Figure 1-1 shows total world energy consumption by energy source, during 1990-2040 (quadrillion btu) [1] Dotted lines for coal and renewables show projected effects of the U.S. Clean Power Plan. The figure clearly implies that the consumption of liquid fuels and renewables should increase to satisfy the energy demand. Petroleum based fuels have been the primary source of energy for transportation needs since early 20th century. In the current scenario of the consumption of transportation fuels, ethanol and biodiesel are the most extensively used biofuels in the transportation sector [1]. Nearly all of the gasoline used in the united states contains 10% ethanol by volume. The U.S. Environmental Protection Agency ruled in October 2010, that cars and light trucks of model year 2007 and newer can use E15 (gasoline with 15% ethanol). E85, a fuel that is 85% ethanol and 15% gasoline, is mainly sold in the Midwest. Biodiesel is usually sold as a blend of biodiesel and petroleum-based diesel fuel. A common blend of diesel fuel is B20, which is 20% biodiesel. The current production of ethanol is 28,059 barrels in April 2016. Corn based ethanol is produced through fermentation with addition of enzymes and ammonia [1].

Another class of biofuels known as advanced biofuels are derived from biomass. Biomass, mainly in the form of wood, is the oldest form of energy used by humans. Traditionally, biomass has been utilized through direct combustion, and this process is still widely used in many parts of the world especially developing nations.

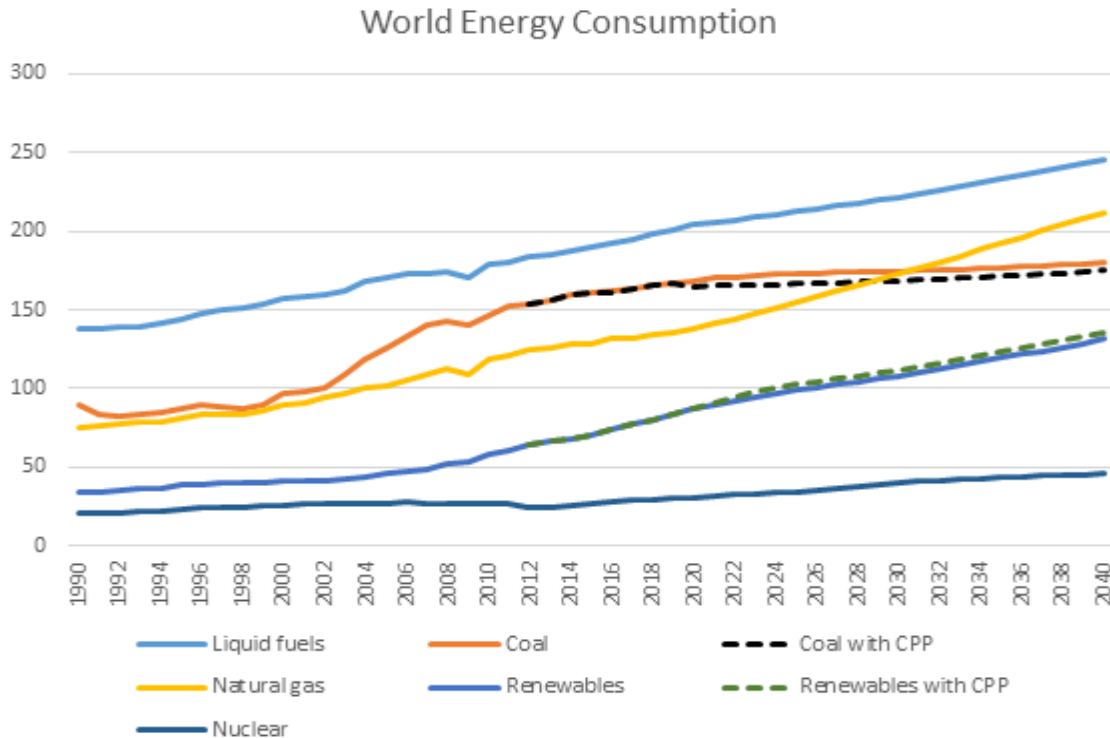


Figure 1-1-Total world energy consumption by energy source,1990-2040 (quadrillion btu) [1] Dotted lines for coal and renewables show projected effects of the U.S. Clean Power Plan.

Fast pyrolysis is the leading technology in which biomass undergoes thermochemical conversion producing bio-oil which looks similar to the to the conventional crude oil and its further fractional distillation results in hydrocarbon fuels compared to the conventional gasoline and diesel can be produced [3].

1.2. Biomass Conversion Processes

The chemical energy in the biomass can be converted into useable energy via different processes. There are several factors which determine the process to be used such as the desired end product, economic conditions, environmental standards, the type and quantity of biomass and project specific factors. Biomass conversion processes are mainly categorized into two types: thermo-chemical and bio-chemical/biological. Primarily there are four important processes of biomass thermo-chemical conversion: direct combustion processes, gasification, pyrolysis and liquefaction. Bio-chemical comprises of two processes: digestion (biogas) and fermentation (ethanol) [4]. The major conversion technologies and processes are discussed in the following sections.

Direct Combustion Processes. It is one of the most basic and simplest form of conversion process, here the burning of biomass such as wood is carried out in presence of air and has been used throughout history. Biomass combustion typically generates temperatures in the range of 800-1000 °C. An important factor is the dryness of biomass, if dryness less than 50% then it not feasible [4]. The energy produces by this process is used for purpose such as cooking, space heating, industrial processes and electricity generation. The main problem in domestic use is the heat loses which is between 30-90%. Net electrical efficiency of biomass power plant is between 20-40%. Higher efficiencies are obtained with systems over 100MW where biomass is co-fired with coal [5]. Due to raw biomasses hydrophilic nature and relatively low heat content compared to most other solid fuels, it is not an ideal choice for direct combustion.

Gasification. Gasification is one of the method for biomass energy conversion process. Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range 800-900°C. The gas produced is known as producer gas or syngas, a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen [3]. The gas produced have low calorific value of 4-6 MJ/N m³ and is used as fuel for gas engines and turbines (LRZ, 1993; Natural Resources Institute, 1996) [4]. High efficiencies (up to about 50%) are available using combined cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine [3].

Liquefaction. Direct liquefaction is a low temperature high pressure process using a catalyst. Though this process yields good quality oil, but the process is complex and expensive as compared to pyrolysis [4].

Fermentation. The process of ethanol production is primarily done by the fermentation process from sugar crops and starch crops. Ethanol can also be produced from cellulosic materials. The biomass is ground down and the starch converted by enzymes to sugars, with yeast then converting the sugar to ethanol [4].

Anaerobic digestion is the fermentation of biomass in absence of oxygen which produces gases primarily, a mixture of methane and carbon dioxide which is commonly known as biogas.

Alcoholic fermentation is the process of decomposition of biomass which contains particularly sugar, starch or cellulose.

Pyrolysis. Pyrolysis is one of the thermochemical processes by which one can convert biomass into higher value products. In this process biomass is heated up in a closed reactor in absence of oxygen and products such as bio-oil, gases, char and other heavy organic compounds are obtained. There are two types of pyrolysis, slow and fast pyrolysis. Slow pyrolysis favors the formation of char and fast pyrolysis favors the formation of bio-oil. Upgrading the bio-oil over specialized catalyst in the presence of hydrogen can give hydrocarbon products which are similar to some extent to the conventional gasoline and diesel but the current methods of upgradation are very expensive. So, this technology can play a role in a bio refinery model to expand the suite of product options available from biomass. The bio-oil produced can be used in automobiles and turbines [6]. There are few problems with bio-oil such as poor thermal stability corrosivity of the oil over which restrict its progress for the use as transportation fuel. As pyrolysis is the main focus of this work, it is discussed in great length in the following chapter.

1.3. Motivation

The adoption of renewable energy is almost inevitably needed to address the drastic climate change effects due to global warming. There are several renewable options, but at the current state of technology and economic market forces no one source can satisfy our energy needs. Biomass has always been the major source of energy for mankind, and currently it is estimated to contribute to the order 10-14% of the world's energy supply.

Biomass can be considered as a potential energy source due to the following reasons:

Thermal energy, electricity and fuels can be obtained from biomass energy. It reduces the carbon dioxide emission. It is renewable source of energy, abundant and can be produced everywhere which helps in reducing the dependency on foreign oils [7].

1.4. Overall Research Objective

The research objectives are decided based upon the literature study. There is continuous improvement in the field of biomass conversion technologies. Research objectives are drafted keeping in mind the addition of new knowledge to the existing one which is very much needed to strengthen the base of biomass conversion technologies. Fast pyrolysis is identified as a potential technology to produce bio-oil and research objectives are based on this specific area.

The overall research objective is to develop and demonstrate a novel paddle reactor for biomass fast pyrolysis, determine its products and investigate the effects of a biomass particle size and reaction temperature on the bio-oil yield. As auger reactor technology is relatively new there exists little data and hence, this study will contribute in the addition of new knowledge.

CHAPTER 2. Technical Literature Review

2.1. State of Art – Fast Pyrolysis

Fast pyrolysis is one of the latest renewable energy processes to have been introduced [8]. The development of fast pyrolysis processes for liquid production has gained much importance in the recent time due to the convenient way of converting low energy value woody biomass into liquid fuels and other useful byproducts [9]. It is defined as the thermal depolymerization and decomposition of biomass structural components, such as, cellulose, hemicellulose and lignin to form liquids, gases and solid residue in absence of oxygen [10]. The fast pyrolysis liquid yield is approximately 70% (dry basis) and it consists of complex mixtures of oxygenated aliphatic and aromatic compounds [9]. There are several factors which play an important role in the distribution and yield of the final products of fast pyrolysis. Certain aspects of fast pyrolysis systems that influence the product distribution and yield are feed drying; particle size; pretreatment; reactor configuration; heat supply; heat transfer; heating rates; reaction temperature; vapor residence time; secondary cracking; char separation; ash separation; liquid collection [11]. Controlling and optimizing these parameters is a very important and tough task in order to get maximum bio-oil yields and optimal product distribution.

The fuel obtained from fast pyrolysis has been successfully tested in boilers, engines and turbines, and have been upgraded to high quality hydrocarbon fuels, although at a presently unacceptable energetic and financial cost [8]. Other emerging areas of utilization are: additives for flue gas cleaning of coal combustion; acetic acid for chip production; adhesives; fuel enhancers; specialty chemicals; and fertilizers [9]. There are several reasons for biofuels to be considered as relevant technology as they include energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to rural sector. The reduction of greenhouse gases is the most important advantage of using biomass energy [12].

The important features of a fast pyrolysis process are as follows [11]:

- Very high heating rates
- Controlled reaction temperatures
- Short vapor residence times
- Rapid condensation of the vapors to form bio-oil

Primarily, there are two main modes of heat transfer: via the reactor heat transfer medium such as the reactor walls in ablative reactors and gas in entrained flow reactors and the other mode is by the heat transfer medium to the biomass. The mechanism of heat transfer in fast pyrolysis is by gas-solid heat transfer in the case of entrained flow reactor via convection and solid-solid heat transfer in the case of fluidized bed reactor via conduction. The fluidized bed reactor system claims to achieve 90% heat transfer to the biomass particles which is fulfilled by good solid-solid mixing [11]. Another important aspect associated with heat transfer is the rate at which the heat is transferred. High heating rate is to be achieved very fast so that biomass particle is completely decomposed and avoiding the secondary reactions inside the biomass particles which are mainly caused by the temperature gradient in the biomass particle.

The size of the biomass particle also plays an important role in distribution of the product. For biomass particle size more than 2mm there is a requirement of char removal. The conductivity of biomass is very poor (0.1 W/mK along the grain and 0.05 W/mK crossgrain) [11]. So, for the large sized particles there is a large temperature gradient inside the particle that leads to the char formation. This char cracks the vapors again into secondary char, water and gas both during the primary vapor formation and in the reactor gas environment. Therefore, to obtain maximum bio-oil yield the secondary reactions are to be avoided and that can be achieved by using grounded biomass small sizes [11].

Reaction temperature is the temperature at which the biomass takes up heat and pyrolyses. For woody biomass decomposition there is a lower limit of reaction temperature of 435°C to achieve at least 50% of bio-oil yields [11]. The maximum bio-oil reported is in the temperature range of 500-520°C [11]. There is difference between reactor temperature and

reaction temperature. The reactor temperature is higher than reaction temperature so as to maintain sufficient temperature gradient between the heat transfer material and the reactor temperature [11].

Vapor residence time is the another important process parameter that is closely related to the bio-oil yield. The shorter residence time would not favor the thermal cracking of the vapors and form solid/gas.

2.1.1 Different Fast Pyrolysis Technologies

In this review different fast pyrolysis technologies are discussed. They are described in brief one-by-one as follows:

Fluidized bed. The solid fuel is fluidized during the fast pyrolysis resulting into a turbulent mixing of the heat transfer material and the biomass. High heat transfer is achieved because the bed contains small sized sand particles of about 250 μm [13]. These units are capable of giving liquid yields between the range 70-75 wt.% from wood on dry feed basis [14]. The biomass particle size should be less than 2mm so as to achieve high and efficient heat transfer because the rate of particle heating is the rate limiting step [14]. Figure 2-1 represents a typical fluidized bed reactor with electrostatic precipitators which are used to collect the solid char particles from the vapors.

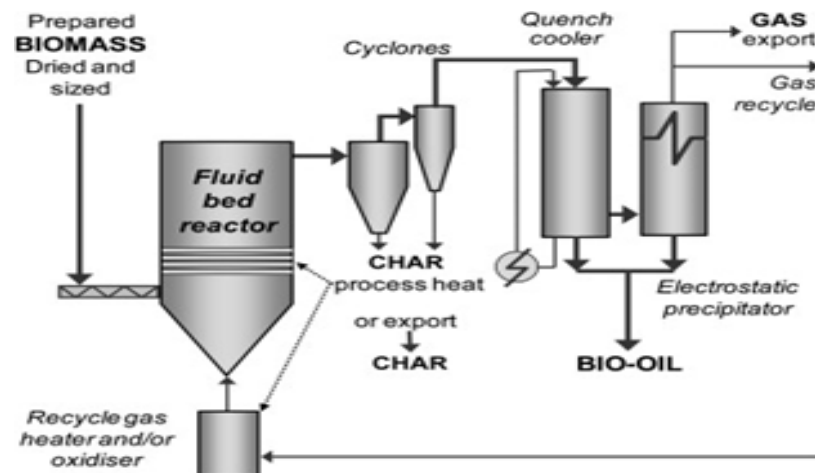


Figure 2-1-Fluidized bed reactor [14].

Circulating fluid bed (CFB). The main working principle of this reactor is same as of fluidized bed technology. Here the mixture of heating material and char is entrained out of the reactor [13]. The mixture is combusted in the secondary combustor, which can be either bubbling or circulating fluid bed, where most of the char is burned [14]. The heating material is then recirculated from the secondary combustor. Heat generated by burning all the char is used to reheat the recirculating heating material. Even though the hydrodynamics are complex, they are used

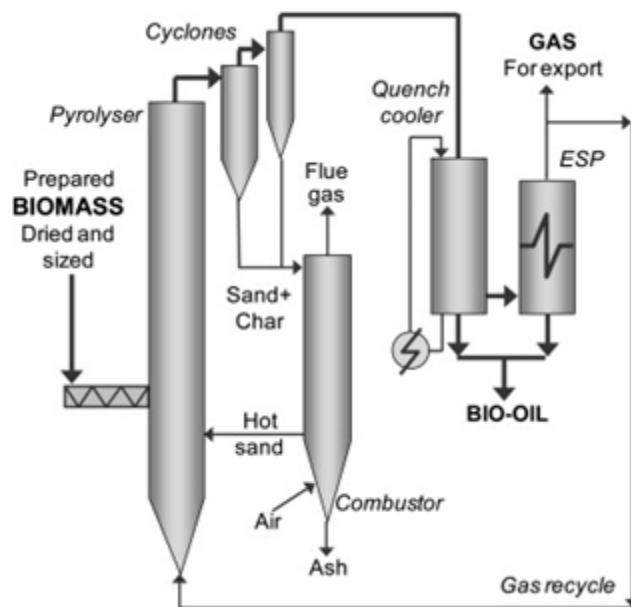


Figure 2-2-Circulating fluid bed reactor [14].

effectively in the petroleum industry. This technology is difficult to scale up and is not proven for good heat transfer at high throughputs [14]. The figure 2-2 shows the process schematic of circulating fluid bed reactor for the recirculation of sand from the combustor to the pyrolyser.

Rotating cone. Intense mixing of heating material and biomass is needed to achieve effective heat transfer. So, high intensity reactor, rotating cone was developed which worked on mechanical mixing of biomass and heating material [13]. Pulverized biomass is fed into the reactor along with the sand via separate feeding lines as shown in figure 2-3. These particles first enter the impeller which is located at the bottom of the heated reactor cone.

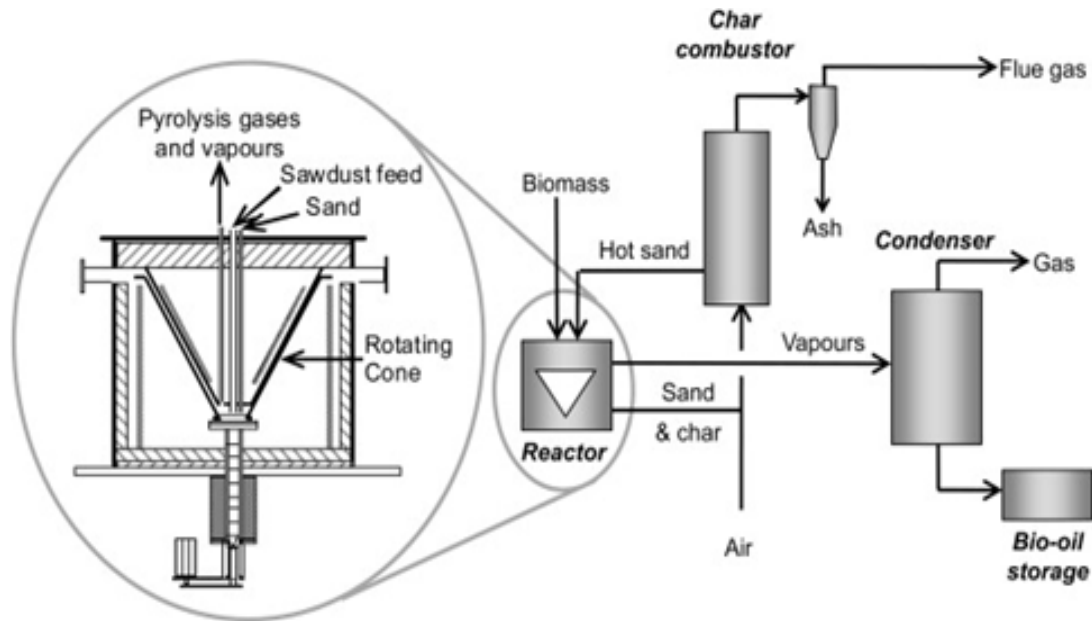


Figure 2-3-Rotating cone pyrolysis reactor and integrated process [14].

After leaving the impeller the particles come in contact with the heated cone and experience high heating rates because of the small distance from the heated surface [15]. From the figure 2-3 it is understood that the vapors rise and leave the reactor while the mixture of heating material and char then enters the separate fluid bed where the char is burned and the sand is reheated and recirculated again in the reactor [14]. Also there is no requirement of the carrier gas, so products of high concentration are obtained [15]. Liquid yields in the range 60-70% on dry feed basis are obtained.

Ablative pyrolysis. In all the other technologies, rate of heat transfer limits the reaction rate and hence, smaller biomass particle sizes are used [14]. It is different for ablative pyrolysis. Ablative pyrolysis could be explained by using this analogy of melting butter in a frying pan and by applying pressure the rate of melting can be increased [14]. Figure 2-4 shows that as the wood pieces come in contact with the heated surface and pressure they start to vaporize. So, opposite to other technologies here large particles can be used. The pressure plays an important role in determining the rate of reaction along with the relative velocity of the wood and reactor surface temperature [14]. This process is limited by the rate of heat supply to the reactor

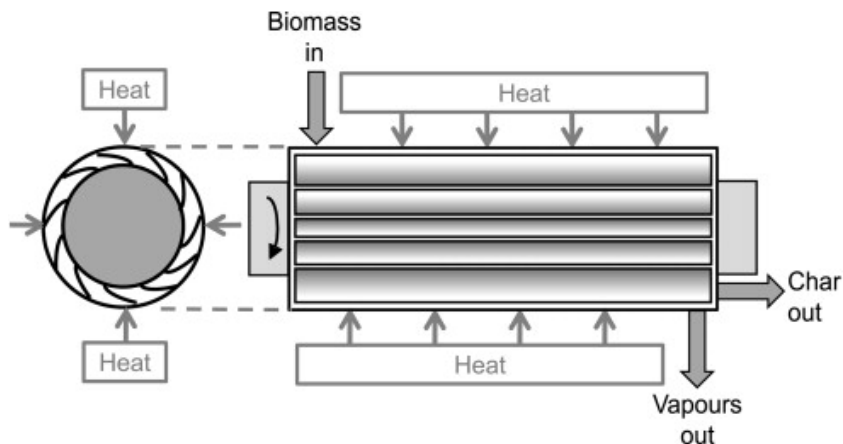


Figure 2-4-Aston University Mark 2 ablative fast pyrolysis reactor [14].

rather than by the rate of heat absorption by the biomass particles. Moreover, the non-requirement of inert gas makes the system compact and intensive. The drawback of this system is scale-up because the heating is controlled by the surface area and hence scaling up will consume lot of space. Liquid yields in the range of 60-65% are reported [14].

Auger reactor. Fluidization of solid fuel particles and heat transfer material doesn't drive this technology. Here, the particles are mechanically driven by a screw. Heat transfer to the biomass particles is achieved by either heating the heat transfer material or by heating the reactor walls and/or the screw. It is difficult to achieve short residence time by this technology, 5 to 30 seconds residence time is achieved based on the reactor size and design [14]. Due to longer residence time the vapors crack down again and thus the liquid yield is less as compared to other technologies. This technology can be scaled up because it overcomes the drawbacks of the fluidizing technology. More information about auger reactor is discussed in detail in further sections.

2.1.2 Commercialization of Fast Pyrolysis Technology

The commercialization of the fast pyrolysis technology was done in 1990 by using fluidized bed concept. Design capacity of 200 kg/h fluid bed was built by Enco Enterprise Inc. in late 1980s and early 1990s by using peat moss to produce liquid fuel [13]. After few years in 2002 a Canadian company, Dynamotive Corporation further commercialized the fluid bed technology of University of Waterloo [13]. The plant began its operation is early

2005 with design capacity of 200 tons per day to provide oil for combustion in Orenda's GT 2500 gas turbine to produce electricity [13].

The CFB technology also commercialized in the early 1990s by Ensyn Technologies Inc. in Ottawa, Canada. The Rapid Thermal Processing (RTP) unit converted woody biomass to pyrolysis liquid which was further used as a source for valuable chemical and fuel [13]. By 2007, eight RTP plants are in commercial operation, ranging from 1 to 100 t/day [13]. The joint venture (JV) between Ensyn and UOP was made to commercialize the pyrolysis technology to produce alternative fuel and generation of electricity [13]. Another JV between Finnish companies Metso and UPM was made to produce bio-oil. The CFB and fluidized bed technologies are developed but the actual operation created problems of erosions and complication caused by the use of seals between various vessels [13].

The initial idea for the rotating cone technology was based on ablative principle without using inert sand which was later modified to sand transported bed rotating cone reactor (RCR) [13]. This technology was developed at University of Twente and was further developed by Biomass Technology Group (BTG) [13]. BTG scaled up Wagenaar's technology to 50 kg/h in 1997 and was further scaled up to 250 kg/h in 2001 [13]. In 2004 the first commercial unit of 50 t/d was sold on so-called name Empty Fruit Bunch (EFB) in Malaysia [13].

The scale up limitation of the fluid bed gave rise to the auger technology. ABRI-Tech, a JV between Advanced BioRefinery Inc, and Forespect Inc. builds units for sale with a capacity of 1 t/d and 50 t/d [13]. The first commercial unit of 50 t/d capacity was built in Iowa in 2009 to produce bio-oil and bio-char from agricultural waste [13].

2.2. Fast Pyrolysis in Auger Reactor

Biomass pyrolysis in auger reactor is an old concept used mainly to produce char coal. Fast pyrolysis in auger reactor is a relatively new concept and is mainly used to produce bio-oil. The bio-oil properties and yields are dependent on the type of reactor used [16]. Many types of reactors such as fluidized bed, ablative, rotating cone, vacuum, auger and free fall are tested for biomass fast pyrolysis but auger reactor has the potential to overcome the

drawbacks of these reactors [17]. Simplicity and compactness of the auger reactor is one of the key feature along with low carrier gas flow requirement [18]. Moreover, continuous batch production and reproducibility is also achieved which proves the effectiveness of auger reactor [18]. Also, on comparing various type of reactors, auger reactor possesses high technical potential and market because of its simple design, low carrier gas flow and can even handle large biomass particles [19].

Fast pyrolysis in auger reactors is gaining attention rapidly because of the advantages it offers over other reactors and that makes it scalable which will further help in achieving the EPA target of producing biofuels within specified timeframe. The most crucial aspect about fast pyrolysis process is to achieve very fast and high heat transfer [20]. The most common methods employed to achieve the desired heat transfer in auger reactor are either by using heat transfer material such as sand, steel shots, alumina ceramic, silicon carbide etc. [21] or by using the heated reactor walls. The walls of the reactor are typically heated by employing multiple band heaters along the length of the reactor [22]. Also sometimes, the reactor is divided into different zones such as the preheat zone and the pyrolysis zone so as to preheat the biomass before entering the pyrolysis zone and hence, enhancing the heat transfer [22]. Another important parameter is the residence time as it controls the distribution of the products. Motors are used to control the rpm of the auger which controls the solid residence time [23]. The vapor residence time depends on the design of the system and is assisted by the flow rate of nitrogen gas as the nitrogen helps the vapors to reach the condenser via convection [24]. It is mainly used to purge out oxygen from the system to produce inert atmosphere [23]. The reaction temperature governs the distribution of the products. Maximum bio-oil yield is obtained at 500°C and the yield decreases as the temperature is raised further [24]. High temperatures favor the production of pyrolysis gases [25]. Next parameter which is to be controlled to obtain high bio-oil yield is the size of the feedstock. [26] showed that rpm and pyrolysis temperature should be optimized to obtain high bio-oil yields for different sizes of feedstock. Auger reactor can accommodate different types of feedstock such as woody biomass, agricultural waste, automobile

shredder residue, tetrapak, spent coffee grounds and many more [25] [27] [20] [22] [24] [23].

2.2.1 Comparison of Different Studies

The following literature discusses about the different types of auger reactors (which are sometimes referred as screw reactors) that have been used till now. There is a wide range of reactors designs, sizes, feedstocks and product distribution. The common configuration of the auger systems is that they consist of feeding units consisting of screws, the main reactor unit which is comprised of a screw, char collector which is connected at the reactor end and a condenser unit which could comprise of multiple condensers. Focus is mainly given toward the auger reactor and less details will be provided for the char collection and condensers which also do not vary much with different systems. The following literature is arranged keeping in mind the timeline of each research work.

One of the early works in 1996 used screw kiln reactor for commercial purpose [28]. The feedstock used was automobile shredder residue with a feed rate of 200 kg/h and a solid residence time of approximately 15 min. Solid residue was collected in a collection pot at the end of the reactor and the vapors were condensed to pyrolytic liquid fraction. The non-condensable gases were either flared or used in combustion for supplying the heat to the screw kiln reactor. The yield of liquid fraction was not high and it was a complex mixture of chemical compounds along with sulfur, chlorine and nitrogen containing compounds hence, it was not possible to use it in automobiles as fuel. Pyrolysis gases were produced which were sufficient enough in energy content and quantity for supplying energy to the pyrolysis process. Another effort was made by the same group in 1999 but the size of the unit was scaled down to laboratory level as shown in the figure 2-5 [29]. The figure explains that the system design is very simple. The feedstock was the same but the feed rate was approximately 100g/h. The pyrolysis temperature range was 500-750°C which gave the rise in pyrolytic gases and the decline in the liquid yield with the increasing temperature. The reactor length was 44.5 cm with the inner diameter of 4.7 cm and was

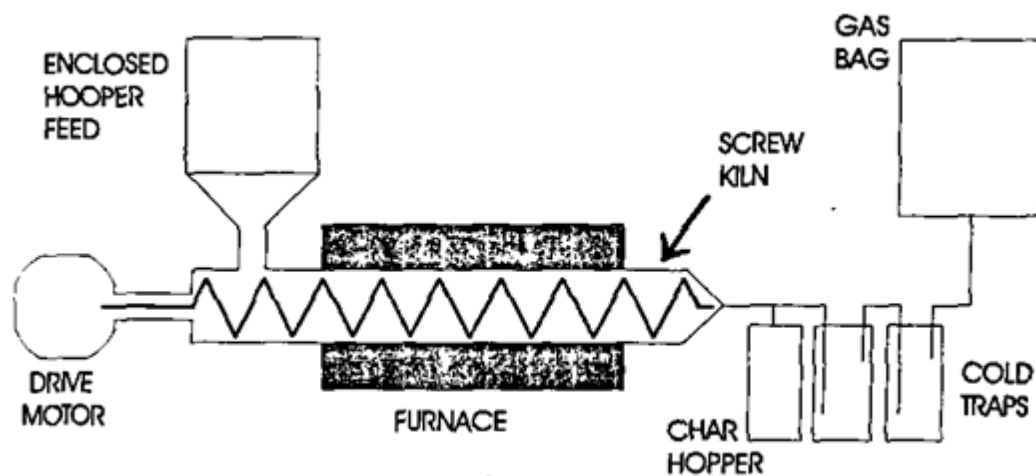


Figure 2-5-Schematic of the screw kiln pyrolysis apparatus [29].

located in center of the Lindberg tube furnace. For most of the experiments performed the solid residence time was about 3.2 min. The solid residue was collected in a collection pot at the end of the reactor and was the major product obtained which was 80% at 500°C and 70% at 750°C and the hot vapors passed through two consecutive cold traps at 0 and -82°C. It was concluded that low pyrolysis temperature around 500°C favored the production of liquids. Since that times till today there has been a significant change in the auger reactor system.

In 2008 pyrolysis of wood and bark in an auger reactor was conducted at Mississippi state university [30]. This pyrolysis unit was claimed as first-generation research prototype and another advanced unit was also designed to provide higher heating rates to the feedstock. For these type of auger reactors high heat transfer and shorter residence time are preferred but here it is different with slower heat transfer and longer residence time. The feed rate is about 1kg/h in a stainless steel proprietary reactor which is common used material for reactors as it can easily handle high temperatures. The reactor diameter and length are 7.6 cm and 102 cm respectively with a rotational speed of 12 rpm at 450°C pyrolysis temperature. No heat carrier material and nitrogen gas was used. The reactor was heated with the help of multiple band heaters along the length of the reactor. Moreover, the reactor was divided into two zones, zone 1 was used to preheat the feedstock at 110-120°C which in turn enhanced the heat transfer rate and zone 2 was the pyrolysis zone at 450°C. The

total residence time from the start of the reactor till the char collector was around 50 s and 30 s in the zone 2. Also, vapor residence time was few seconds (exact number not reported) and vapors were condensed in a proprietary condenser. The bio-oil yield for the feedstocks tested were in the range of 40-60% and the yields of char were in the range of 9-30%, non-condensable gases yield was not measured.

In 2011 several studies contributed to the pool of knowledge in this field by using different type of feedstocks in novel auger reactors [17] [24] [26]. Douglas fir wood was used by [17] to study the effect of temperature on the bio-oil yield. Feed rate was about 600-720 g/h in a stainless steel tube, diameter of 10 cm and length of 58.5 cm enclosed in a Lindberg/Blue M furnace which are common lab scale reactors design parameters. No heat carrier material was used and the heat was transferred by the heated reactor walls. Large temperature gradient between the heated walls and the biomass bed was observed because of the inefficiencies of heat transfer between them. This design gave the solid residence time of 1 min at 13 rpm auger speed which was fixed for all the experiments. Nitrogen was used as carrier gas at 20 L/min and the calculated vapor residence time was about 8 s. The condensable vapors were passed through 3 stages of condensation process. The first condenser was typically used vertical tube with cooled water coils which brought down the vapor temperature to about 24°C. The second condenser system consisted of 4 trapping units buried in ice bath and the last one was a bubbling trap with water which was cooled by ice. This systematic condenser system ensured that all the condensable vapors are converted to bio-oil. Maximum bio-oil yield was about 59% and it is reported that the bio-oil results are comparable to the yields obtained from the fluidized bed reactor which has approximate bio-oil yields greater than 60%. The non-condensable gases were not measured and were calculated by mass balance. Another study demonstrated a novel auger type which consisted of a single tapered screw extruder [26]. The diameter of the screw increased gradually from the start by 2° taper such that the gap is reduced. With the increasing diameter, increase in the grain size and high feed rate, the feed was crushed which further broke the hot char and exposed the grain surface, favoring the pyrolysis reaction of biomass. This concept decreases the secondary reactions with increased liquid

yields. This study showed that for a particular range of particle size with the corresponding rpm gave the optimal pyrolysis temperature that resulted into high bio-oil yields. At 20 rpm for 0.425-1.18 mm the bio-oil yields ranged from 50-57% and at 40 rpm for 1.7-3.35 mm the yields were 56-60%. Pyrolysis of forestry waste was investigated using auger reactor by [24]. The length of the reactor was 30 cm with internal diameter of 2.54 cm. This is one of the smallest reactor sizes amongst various studies. No heat carrier was used; heat was supplied from the heated walls. Nitrogen at 5NL/min was used to purge and helped the pyrolysis vapors to reach the condenser via natural convection. Different parameters such as reaction temperature, solid residence time and mass flow rate were investigated. Finally, it was concluded that 773 K is optimal reaction temperature for maximum liquid yield with reaction time as 2 min to be sufficient for complete pyrolysis. This study supports for the scaling up of the auger reactor because of its simple design and no pre-treatment of feedstock is necessary and promotes the concept of mobile auger reactors.

In 2012 a two stage screw kiln reactor was used by [20] for the production of synthesis gas (syn gas). The first stage comprised of fast pyrolysis in auger reactor and the next stage did the catalytic steam reforming of pyrolysis gases. The design of this system as shown in figure 2-6 is similar to the design as shown in figure 2-5. But there is a difference that this reactor is two stage. Waste woody biomass was used as feedstock sized about 2.8-9 mm at feed rate of 240 g/h with a solid residence time of 40 s. the size of the feedstock is larger than what is typically used, 2mm. The design parameters of the screw kiln were 6.2 cm in diameter and 54 cm long which was made of stainless steel. The screw kiln was heated at a rate of 40°C/s with the help of electric furnace to 500°C. Nitrogen was used to purge the system and assist the pyrolysis vapors in flowing through the system. After all the pyrolytic gases passed through the second stage all the condensable were collected after condensation and the non-condensable gases were passes through the activated carbon filters and collected into sampling bags. The setup showed an increase in the amount of hydrogen gas in the presence of the second stage which consisted of the catalysts.

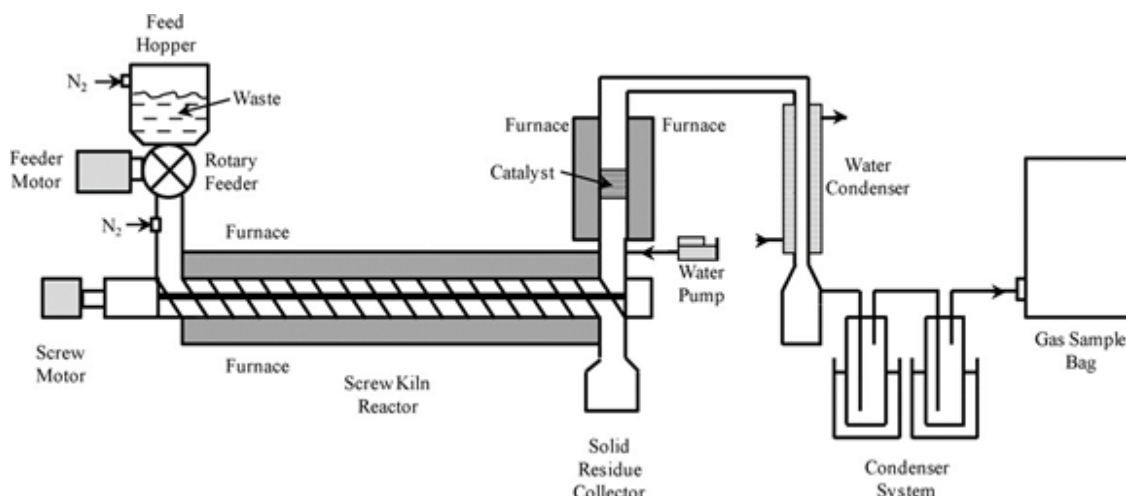


Figure 2-6-Schematic diagram of the continuous feed screw-kiln pyrolysis-gasification/catalytic steam reforming system [20].

In 2013 aseptic packages (tetrapak) were used as feedstock in a screw reactor [25]. The reason for using that feedstock was that it is present in high proportion in MSW (Municipal Solid Waste). It is observed that the overall design of the system does not change if we compare figures 2-5,6,7. Average feed rate was about 100 g with a residence time of 150 s. Two reactors, externally heated were used in line, the first pyrolysed the feedstock and the second one did the catalytic tar decomposition to favor the gas product as shown in figure 2-7. The diameter of the first reactor was 25 mm which is very small compared to other literatures and the length was 300 mm. the second reactor also had the same dimensions as the first one. The aim of the experiments was to maximize the gas yield and also lowering the tar content within the temperature range of 650-850°C. With the increasing temperature and secondary tar cracking using the catalysts the proportion of gas increased. Moreover, the effect of catalyst was significant above 750°C hence, it was concluded that this type of reactor has potential to convert tetrapak into useful energy source. In the same year, one of the research work conducted fast pyrolysis of agricultural waste (cassava rhizome) as a feedstock in counter rotating twin screw reactor unit [16]. The important aspect of this system is that they used sand as heat carrier. The feed rate of biomass and sand were 380-400 g/h and 2kg/h at 9 rpm and 27 rpm respectively. Also, the twin screw reactor was an added advantage for better heat transfer. Outer diameter of each

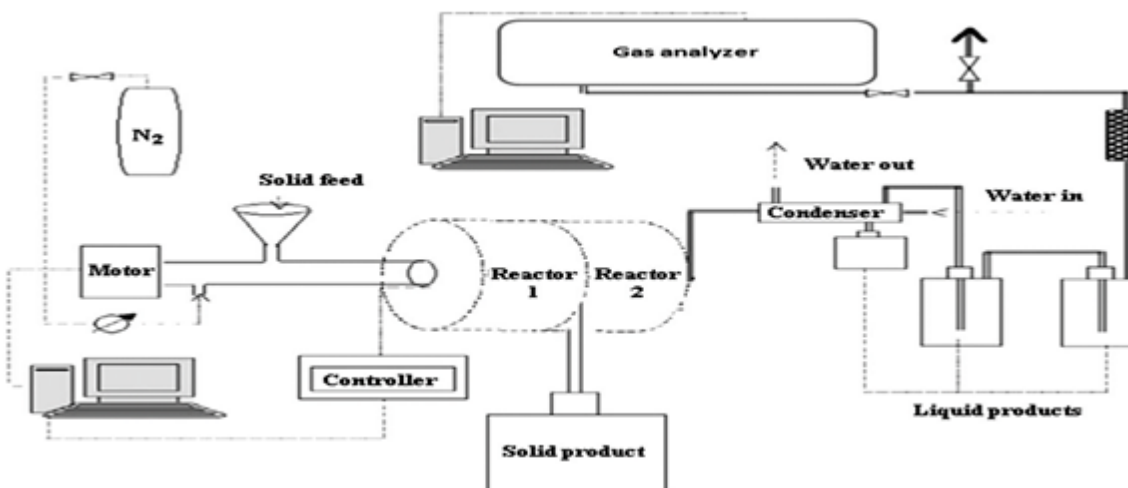


Figure 2-7-Scheme of laboratory pyrolysis unit [25].

screw was 25 mm (about 1”) and were 450 mm long (about 18”). Various biomass sizes of <0.250, 0.250-0.425 and 0.425-0.6 were used along with sand sized 0.425-0.6 mm.

The temperature of the auger reactor was varied from 500 to 700°C while keeping the sand temperature constant at 500°C. The sand is introduced first in the reactor which in turn supply the heat to the biomass entering afterwards. Another parameter varied was nitrogen flow rate which was constant for biomass and sand hopper at 2 L/min while the flow rate at the auger reactor was varied from 4 to 7 L/min. It was concluded that the optimal temperature for maximum bio-oil yield was 555°C and the optimal biomass particle size was 0.250-0.425 mm with the nitrogen flow rate and pressure at 4 L/min and 2 bar.

In 2014 similar concept of using two reactors one (auger) for pyrolysis and second (fixed bed) for the catalytic upgradation as seen in figure 2-8 [31]. This concept is similar to the study previously discussed by [20]. Pine wood shredded to <1 mm was used as feedstock at a rate of 25 kg/h. The residence time was 8 min at 5 rpm for all the tests for the reactor diameter 16 cm and length of 300 cm in which 240 cm was the actual heating zone. It was heated by external means. Comparing the figures 2-6 and 2-8 the design is similar consisting of two stages. There was a significant temperature gradient of 100°C between the reactor wall and the biomass samples which exposes the inefficiency of not using a heat carrier material. The yields of bio-oil and the gases were not reported but comments about the trends were made.

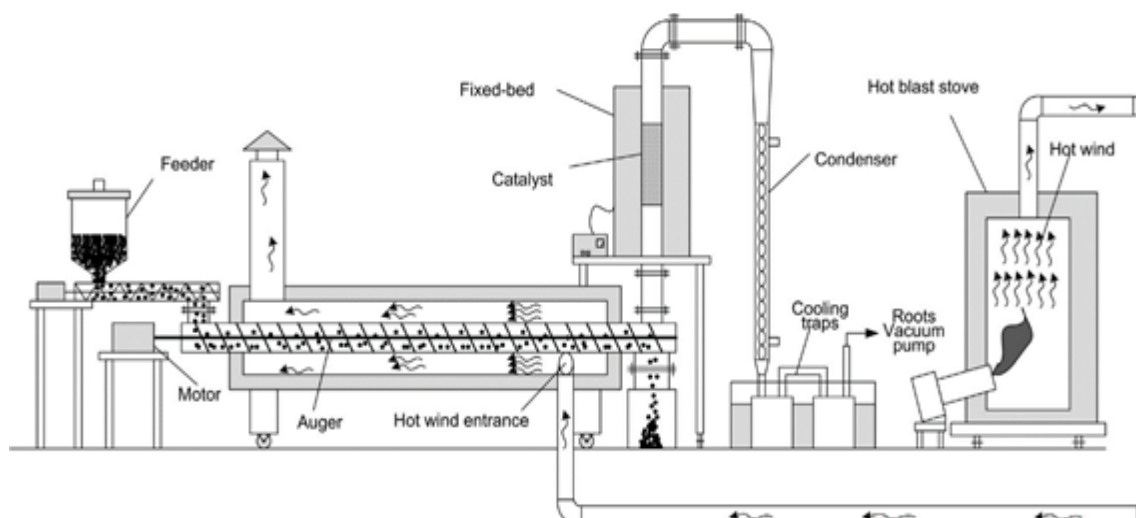


Figure 2-8-Scheme of a combination of auger pyrolysis reactor and fixed-bed catalytic reactor [31].

The combined system is better than fluid bed as no carrier gas needed and no mixing of the catalyst with the biomass is needed. So, this system showed improvement in bio-oil quality with simultaneous reduction in the oxygen content via catalytic upgrading.

The variety of feedstock is increasing rapidly. In 2015 investigation was done on the use of spent coffee beans in a screw conveyer reactor as shown in figure 2-9 [23]. The screw reactor used was a novel reactor with a decreasing flight depth from reactor inlet to outlet which presses the biomass to the reactor and hence enhancing the heat transfer. Although this concept is previously used by [26]. The feed capacity was about 1-6 kg/h but only 1-1.5 kg/h feed rate was employed. No heat carrier was used and heating was achieved by the employment of 6 consecutive band heaters which were virtually divided into 3 heating zones. The first two zones were set at 200 and 350°C respectively to achieve the pre heating which further supports the heat transfer in the pyrolysis zone which is set and varied in the range of 450-550°C. The solid residence time was estimated with the help of the screw rotation speed (45-75 rpm) in the range of 23-42 s. Two successively placed condensers at 25°C and -7°C condensed the vapors and it were collected into glass jars. Positive bio-oil yields of 61.8% (maximum) were reported at 500°C with maximum char yield of 20.6 % at minimum temperature of 429°C. Observations made were regarding the increasing the auger rpm resulting into reduced residence time which gave value of maximum bio-oil yield of 61.7%, estimated by the model (response surface methodology). The quality of the bio-

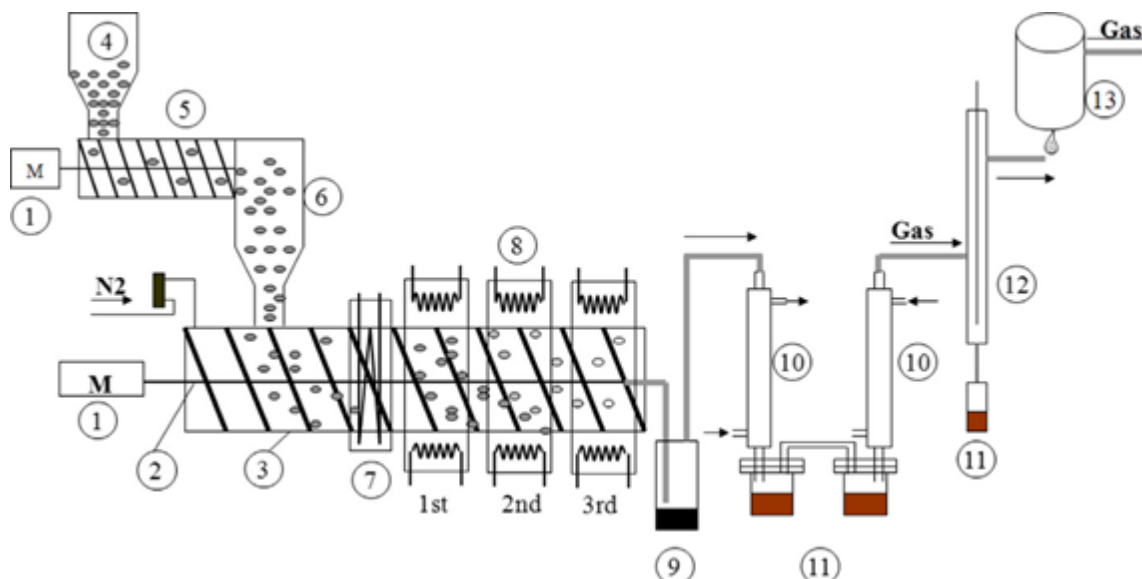


Figure 2-9-A schematic of the screw-conveyor pyrolysis reactor and downstream equipment. 1. Motor, 2. screw conveyor, 3. pyrolysis reactor, 4. biomass feed hopper, 5. auger feeder, 6. feeding connection, 7. cooler, 8. heating zones, 9. char collector, 10. condenser, 11. bio-oil container, 12. electrostatic precipitator, 13. gas flame calorimeter. [23].

oil obtained was better as compared to other studies and hence, spent coffee grounds prove to be a potential feedstock for bio-oil production.

In 2016, fast pyrolysis of lignocellulosic was performed in a twin screw mixer reactor as shown in the figure 2-10 [32]. The feedstocks included hard-wood, soft wood, wheat straw and wheat bran with a throughput of 6-16 kg/h. Sand/stainless steel balls were used as a heat carrier material at 550°C. Heat carrier is introduced later in the reactor with the biomass which is already preheated. The heat carrier flow rate is about 1.5 t/h with a fill ratio of 0.5 in the reactor. Fill ratio more than this is not recommended due to the plugging issues. This twin screw reactor gave high yields of 65 +/- 10 wt% with woody biomass and 50 +/-10 wt% with cereal straw.

All these studies discussed till now prove that they are approaching the bio-oil yields as obtained from fluid bed. Keeping in mind the advantages of auger/screw reactors, scaling up is possible which will help in achieving our goal of producing bio-oils in high quantities and supporting the targets of EPA. From table 2-1 one could compares all the above mentioned studies with respect to the design

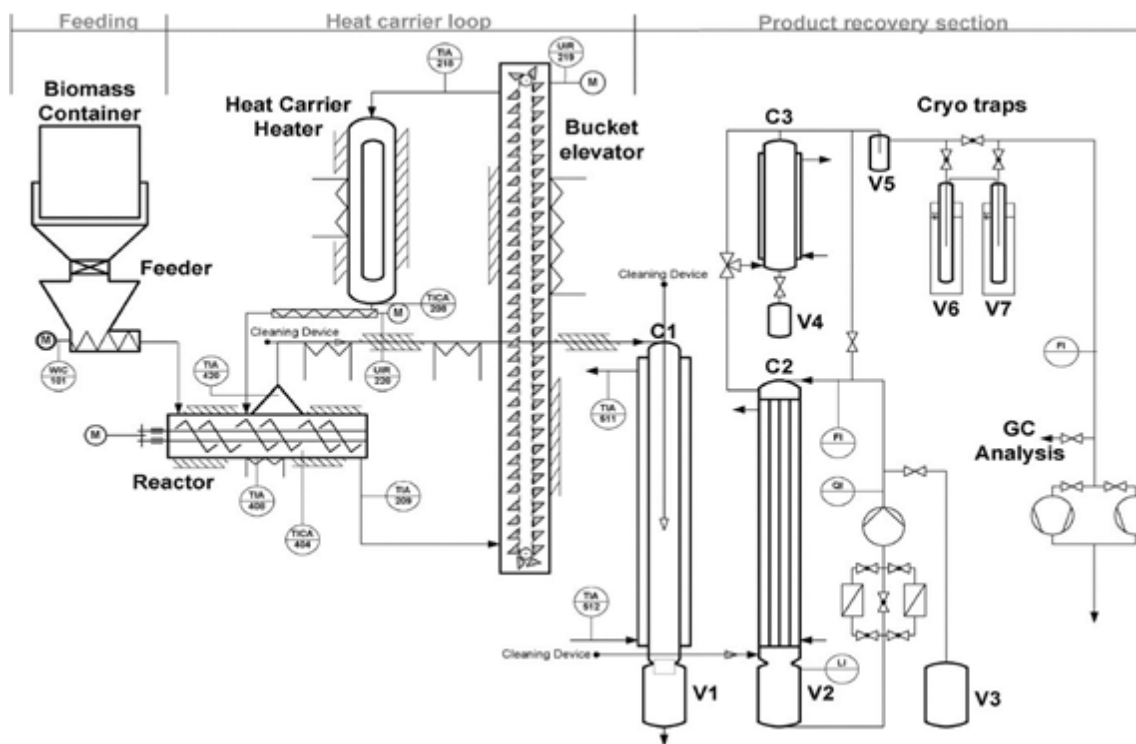


Figure 2-10-Simplified flowsheet of the fast pyrolysis process development unit (PDU) [32].

Table 2-1- Parametric details about the different auger reactors.

Feedstock	Biomass Feed Rate (g/h)	Reactor Type	Reactor Diameter (cm)	Reactor Length (cm)	Residence Time (min)	RPM	Heat Transfer Material	Pyrolysis Temperature (°C)	Main product	Year	Yield (%)
Auto shredder residue	100	Single screw	4.7	44.5	3.2, 11.6	-	-	500-750	Solid	1999	70-80
Wood& Bark (pine&oak)	1000	Single screw	7.6	102	0.5	12	-	450	Liquid	2008	40-60
Douglas fir wood	600-720	Single screw	10	58.5	0.5	13	-	500	Liquid	2013	59
Camphor tree	2000, 3000	Tapered single screw	-	-	-	20-40	-	400-550	Liquid	2011	50-60
Forestry Waste	3.9, 4.8, 6.9	Single screw	2.54	30	1.5, 2, 3, 5	-	-	500-800	Liquid, gases	2011	35-60, 15-50
Waste wood	240	Single screw	6.2	54	0.66	-	-	500, 760	Gases	2012	49-54
Tetrapak	100	Single screw	2.5	30	3.0	-	-	650-850	Gases	2013	55-80
Cassava Rhizome	380-400	Twin Screw	2.5 each screw	45	-	9	Yes	500-700	Liquid	2013	30-50
Pine wood	2500	Single screw	16	300	8	5	-	400-600	Gases	2013	20-45

2.3 Research Objectives

The research objectives are decided based on the primary literature review done in this field. With the help of the thorough literature review and preliminary trials the main research objective decided was to conduct experimental investigations of specific type of energy crop (Arundo Donax) in a novel paddle reactor. This thesis will present data for a new fast pyrolysis feedstock in support of achieving fast pyrolysis in a novel mixing auger reactor. Following are the explicit research objectives.

1. Review current auger technology and demonstrations
2. Demonstrate the operation of a novel paddle reactor developed at MTU (Michigan Technological University) using Arundo Donax as a feedstock
3. Study and analyze the effect of reaction temperature and biomass particle size on the yields of bio-oil
4. Determine the optimum temperature and biomass size and recommend conversion schemes for best bio-oil yield
5. Identify the potential changes and improvements in the current system for further improvements for scaling up

CHAPTER 3. Experimental Methods and Working

3.1 Introduction

This chapter discusses the experimental setup in detail, components and its development, working of the system and test matrix. Figure 3-1 shows the fast pyrolysis system used in this research. The main components are biomass hopper, heat transfer material hopper, reactor, char collector and a water cooled condenser. Overall, biomass and heat transfer material (HTM, such as sand) are the inputs in the system and char, bio-oil and pyrolysis gases are system outputs that are collected in bio-oil condenser, char collector and bio-oil collection bottle. The permanent gases exit the system through a vented hood, and were not collected. The auger reactor is the heart of the system, and is where the conversion takes place. There are also two additional augers which act to meter the biomass and HTM into the reactor. All components and their development will be discussed in detail in the coming sections.



Figure 3-1-Fast pyrolysis unit at MTU.

3.2 Methods and Materials

3.2.1 Components of Lab Scale Setup and Its Development

Biomass Feeding System. The hopper used for biomass feeding is simple in design and working. It was initially designed by studying the capacity of the system. With the help of the literature review we have analyzed the parameters such as reactor size and the throughput it can handle. So 100 g/h was decided as the flow rate. Nitrogen gas line were connected to the biomass drop tube to create a positive pressure and prevent the backflow of the pyrolysis vapors. Another important parameter was the filling factor of the auger. It is defined as the volume occupied by the solids in

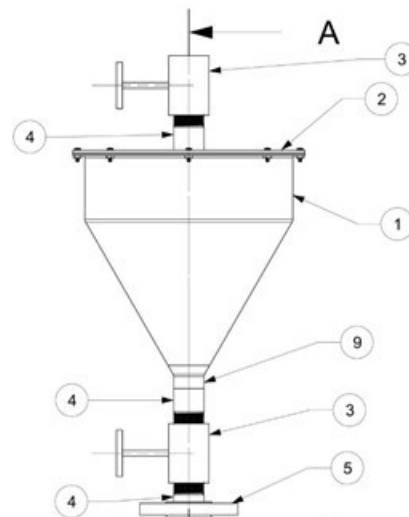


Figure 3-2-Biomass hopper initial design.

the reactor. Online literature from auger manufacturers (for example Martin Sprocket and Gear, <http://www.martinsprocket.com/>), typically rate the auger fill properties based on their flow characteristics. Well behaved flow of granular solids with small diameter are generally rated around this filling factor of 0.45. The calculated value was about 0.45, that means approximately half of the reactor is full which will be pre dominantly the lower half as the input materials are solid and the upper half will contain carrier gas and vapors generated from the fast pyrolysis reaction. The biomass auger which was a simple screw auger was driven by $\frac{1}{2}$ HP motor. The 1" drop tube connected the end of the biomass feeding system to the reactor biomass inlet. They had a flange connection in the middle. The length of the drop tube is long enough so as to prevent heat from conducting back to the raw biomass and starting the reaction before it is intended. The biomass auger housing was 1" in diameter, auger shaft (the inner cylinder around which flights are cut) was 0.5" with normal flights without paddles, diameter to pitch ratio was 1 and the working length was 6". The initial design of the hopper is as show in the figure 3-2, as was a conical shaped hopper with a flange connection with the inlet port of the reactor. Valves were included on



Figure 3-3- (Starting from left to right)-The old hopper with agitator, The old agitator with a bend and The old agitator.

either end of the hopper to allow material to be added while the system was heated, and allow for inert purging before feeding resumed. Due to some plugging problems faced modifications were made in the old auger which are describes in the following section.

The problem that we faced was of clogging. The proposed method of flow was based on gravity, but due to the inter locking nature of the biomass grains the flow gets plugged and the material compacts. It was noticed that particles which were uniform in size i.e. more spherical or cubic (opposed to particles with long aspect ratios) and possessed good flowability had no problem in flowing through the vertical process tubing. It is important to note that the mechanical augers never experienced plugging or locking due to biomass particles, however we encountered the biomass particles interlocking and bridging when gravity was relied on alone to promote the flow. The initial design had an agitation system as shown in figure 3-3 and it proved to be a good fit for lower rpm where material flow rate was very low. When the mass flow increased, however, the vertical drop tube as shown in figure 3-4 was bridged/filled and the agitator was unable to rotate and break the bridging of the biomass and ultimately got bent due to the resistance provided by the plugged biomass. The mouth of the hoppers (both the HTM and biomass) were elongated at the joining with the feeding auger to allow the biomass to enter the auger more freely.



Figure 3-4-(Starting from left to right)-Modified dosing auger body for new feed hopper, modified feed hopper with 75° inclination and new agitator.

The changes made for the new auger housing was done by cutting out slot of 1 by 3 inch in the auger housing as seen in figure 3-4 so as to give more broad and long feeding face. Then several stainless steel strips were welded near the inlet side of the auger as seen in figure 3-5 so as to decrease the height of the flights and decrease the flow rate to the drop tube and prevent plugging of biomass. Also the wall inclination of the new hopper was made 75° to achieve stable flow which can be seen from figure 3-4. The flow rate test was performed in cold conditions with new agitation system and it was stable and continuous without any problem of plugging.



Figure 3-5-Modified dosing auger.

Heat Transfer Material Feeding System. The HTM hopper is identical to the biomass hopper. There is no agitation system as sand was used as HTM and it has excellent flowability. Similar ½ HP motor with a variable frequency drive was used to control the flow rate of sand. Similar to biomass feeding system nitrogen line were connected to the drop tube. The flow rate is discussed in further section.

Reactor. The reactor is the heart of the system where the fast pyrolysis process takes place. It is made of stainless steel tube of diameter 1", thickness of 0.12" and 18" of length. The diameter of the reactor shaft which is a combination of cut flight auger and paddles is 0.5", the height of the flights is 0.24" so there is a minimal of 0.02" between the auger and the reactor housing. The diameter to pitch ratio is ½, where diameter is of the reactor housing. Also, there are 4 paddles in between every pitch as seen in figure 3-7. The reactor is externally heated by electric means. Figure 3-6 shows the twelve band heaters with a capacity of 250W each are used and are spread over a length of 18", 8 bands to heat the HTM preheat zone and 4 to heat the 6" of the pyrolysis zone. Twelve K-type thermocouples were attached at the bottom of the reactor in tandem with each of the band heaters to obtain/control the HTM temperature and the reaction temperature precisely. The thermocouples were placed through the wall of the reactor, so the thermocouple extended past the wall of the reactor slightly and directly contacted the material. This minimized the convolution with the wall temperature.

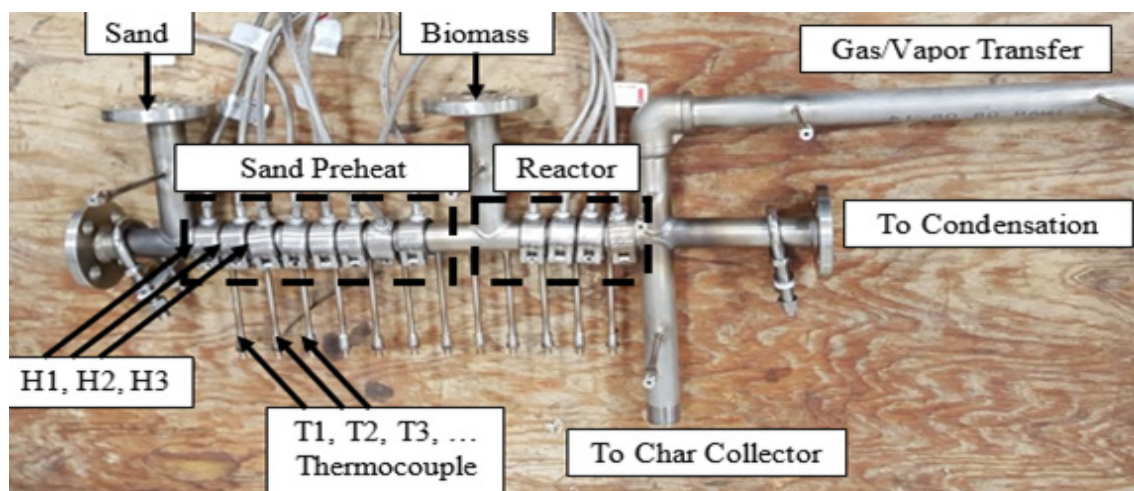


Figure 3-6-Reactor body of the fast pyrolysis system.

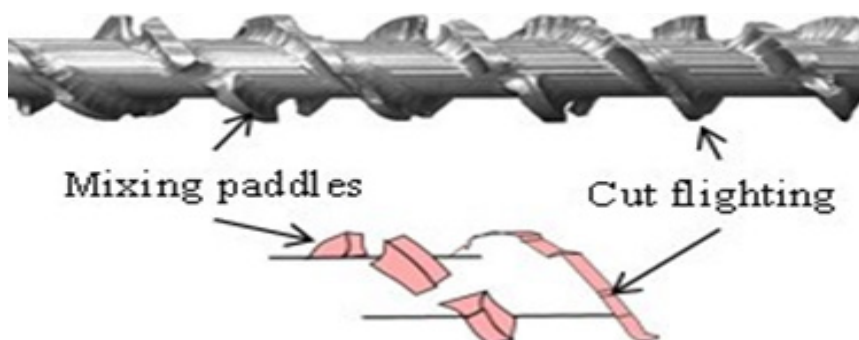


Figure 3-7-Detailed image of the well mixed reactor.

The reactor was insulated with mineral wool such that the external surfaces were approximately ambient temperature and retained sufficient process heat.

The use of this novel paddle reactor was done to achieve better mixing (as discussed in previous chapter). The cut flights make up 40% cut area through which the material is left behind and gets mixed with the oncoming material. Four paddles were placed at 45° to the



Figure 3-8-Shell tube heat exchanger with baffles on the tube side.

shaft in each pitch. The paddles are used to move the material sideways and forward both such that high level of mixing is achieved. Combination of cut flight and paddle both enhances the mixing phenomena.

The reactor cannot be defined as a traditional auger as it has cut flights and paddles which do not completely move the material forward as in augers. Moreover, the residence time in the reactor cannot be calculated by the relation between number of pitches and motor speed. So the concept of effective pitches was put forward which will be discussed in further section

Products Collection System. The product collection systems consist char and sand collector for the collection of solids and condensing units for the collection of the liquids. The condensing system used is a simple tube and shell type heat exchanger with baffles as shown in the figure 3-8.



Figure 3-9- (Starting from left to right)-The condenser image, scrubber and tube side of heat exchanger with condensed bio-oil on the top.

Figure 3-8 and 3-9 shows the inside and assembly view of the heat exchanger respectively. The condenser had three tubes for the incoming pyrolysis vapors from the tube side and from the shell side the cold water flows at around 20°C. The baffles as seen in figure 3-8 creates turbulence which further helps in uniformly taking out heat from the tubes.

Figure 3-9 represents the scrubber. It is the last condenser junction where the condensable will be trapped before finally exiting the system. Scrubber is kept in an ice bath at around 5°C.

3.2.2 Biomass Preparation

Arundo Donax was used as biomass for the experiments. No pre-treatment was done to the biomass. The initial material was stored outdoors on the farming site and was sent to MTU via a super bag (~300kg). The initial size was too big as shown in figure 3-10, and was size reduced to less than 1mm with a rotor grinder. Due to the outdoors storage, a high moisture content was initially present in the material. The Arundo Donax was dried at 150°C to remove moisture and kill any biological contaminants on the biomass. Aluminum tins were used, and were filled approximately half as shown in the figure 3-10. After it was dried in oven, moisture test was done and it was dried till no change in weight was observed. The moisture content was approximately between 3-5% wt. and then the biomass was grinded. After that 3 different sizes were sieved as shown in figure 4-4. After that they were stored in sealed plastic bags and placed in air tight buckets. Refer appendix B for the details of the equipment and instruments used for biomass preparation.



Figure 3-10- (Starting from left to right)-Arundo Donax drying on the oven, raw Arundo Donax and grinded and sieved Arundo Donax.

3.2.3 Calibration of The Setup

Calibration of the complete setup was done in both cold and hot conditions. The initial calibrations were done in cold conditions. Calibration of feed rate of biomass and HTM was done to ensure proper system throughput and motor conditions. The flow rate of each biomass type has to be done as the densities and particle size play an important role in mass flow and also because of the small size of the system. Arundo Donax (A.Donax) was used as biomass. For this test the hoppers were filled and flooded feed mode was used.

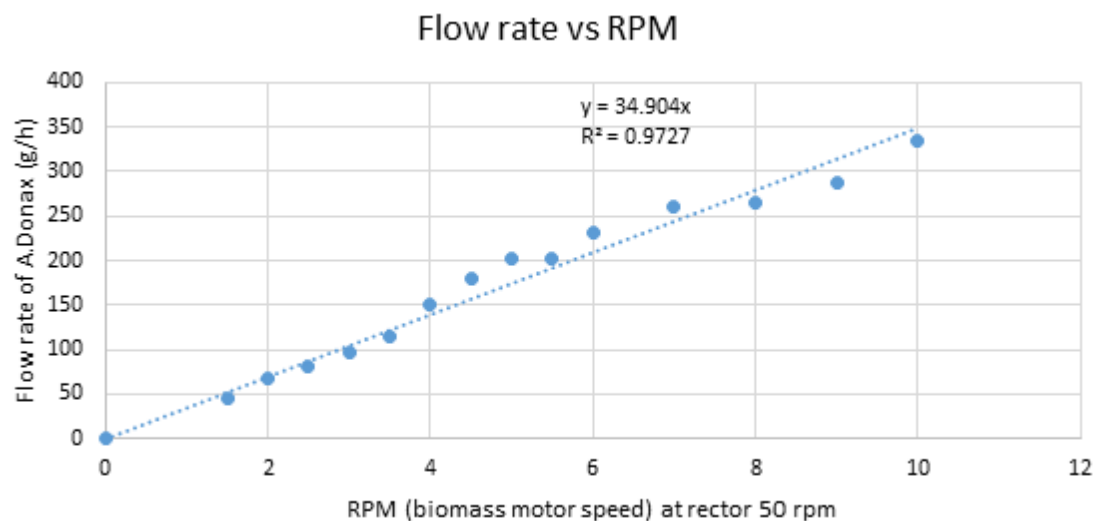


Figure 3-11-Biomass dosing auger calibration with Arundo Donax.

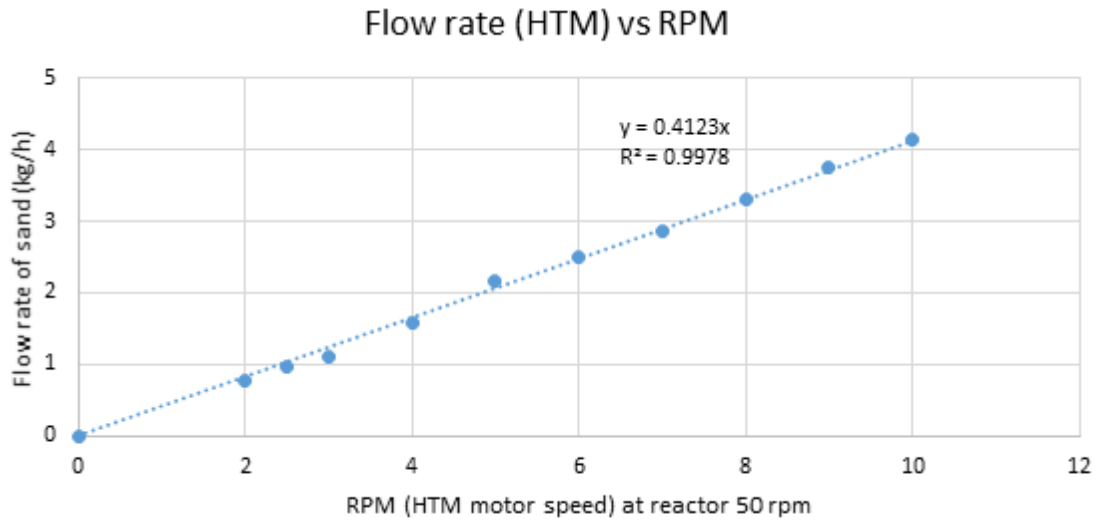


Figure 3-12-HTM dosing auger calibration with sand.

This test was done by removing the char collector and placing weighing balance at end of the reactor exit tube. Mass flow rate of biomass was measured for different motor speeds (RPM) and were plotted against motor RPM as show in the figure 3-11. Also the residence time was evaluated by the relation between time, pitches and rpm of motor. The relation is $t_{auger} = C_{auger} * v$ where t_{auger} is the residence time in the biomass auger, C_{auger} is the number of pitches and v is the rpm of the dosing auger. There are 3.5 pitches from the inlet to outlet of the feeding auger system. The reactor rpm was 50 for all the calibration tests.

From the figure 3-11 it is clear that flow rate of 100 g/h can be achieved at approximately 3 rpm motor speed. Though we had an agitation system which helped in attaining stable flow, external agitation with a rubber mallet was occasionally needed approximately every 15min to ensure that biomass was not bridging. The R^2 value of 0.97 shows strong relation from the above data, and establishes a proper calibration for setting feed rates values. It is important to note that this feed rate (RPM) was used to be consistent between experiments, and was not used for mass balance purposes (due to the occasional bridging instances).

In this research sand was used as HTM. Cold condition calibration was performed similar to the biomass calibration. In cold conditions sand flowed very stable and no agitator or hammering were needed. Mass flow rate vs motor rpm graph is shown in figure 3-12. It is

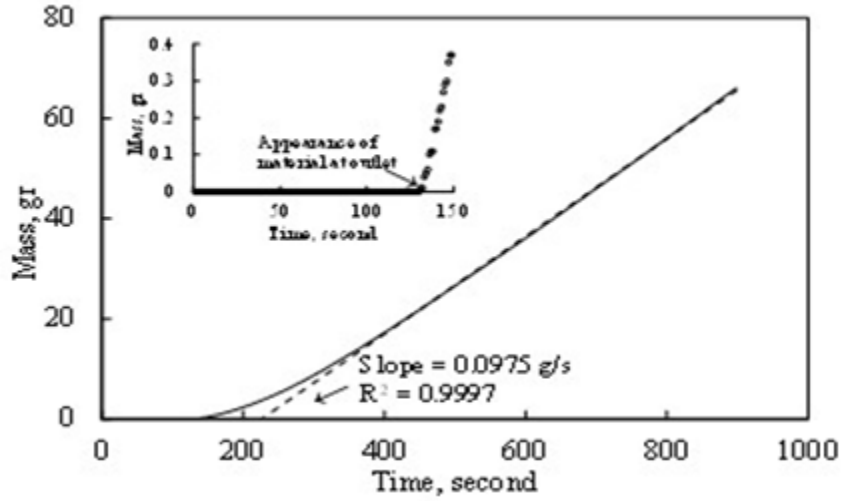


Figure 3-13-Biomass flow rate at 25 RPM.

evident from the figure that the flow was very stable and 4 rpm was selected as the sand flow rate value of about 1.6 kg/h is obtained. The number of pitches are same as both the feeding systems are identical so the residence time will also be same.

The residence time in the reactor could have been measured easily but normal screw auger used was not the typical screw auger in the reactor, it was modified one so a different approach was used. The time taken for the biomass to reach the reactor end from the HTM hopper was measured which comprised of the residence time (t_{reac}). The residence time in the preheat zone and the pyrolysis zone are calculated by the equation used for normal screw augers but we need to consider the effect of inefficiencies in conveying in the current auger reactor. Because of the cuts and the paddles, the modified auger requires more revolutions to move the material one equivalent pitch in a traditional screw.

$$t_{tot} = \frac{C_{HTM}}{v_{reac}} + \frac{C_{pyr}}{v_{reac}} = \frac{(C_{HTM} + C_{pyr})}{v_{reac}} = \frac{C_{reac}}{v_{reac}}$$

where t_{tot} is the summation of the residence times of the preheat HTM zone and the pyrolysis zone. C_{HTM} and C_{pyr} are the effective number of pitches in the preheat zone and the pyrolysis zone respectively. v_{reac} is the rpm of the reactor. So the C_{reac} is equal to the summation of C_{HTM} and C_{pyr} which will give us the total number of pitches. The pitch to diameter (1") ratio is 2 and the total length of reactor is 18" so the number of pitches in the reactor will be 9 but due to the cut flights in auger and the additional paddles the material

flows backward and slows down which is equivalent to increasing the number of effective “*pitches*”. So, the number of effective pitches should be more than normal number of pitches. The method to determine the effective number of pitches is by finding out time taken by the material to reach from the hopper to the reactor outlet.

The figure 3-13 shows the time taken from the HTM hopper till exit of the reactor and also the mass flow rate for various experiments carried out. Figure shows the typical measurement of these experiments, the appearance time of the material from hopper to the end of reactor (in the inset of the figure) and the mass flowrate (main plot). After the residence time is accurately obtained, the number of effective pitches could be determined by the help of graph as shown in figure 3-14 which is between residence time and inverse of rotation frequency. The value of c_{reac} found was 39.15 pitches and c_{pyro} was 6.04 hence, $c_{\text{HTM}} = c_{\text{reac}} - c_{\text{pyro}}$ gave us value of 33.11 pitches as compared to calculated value of 6

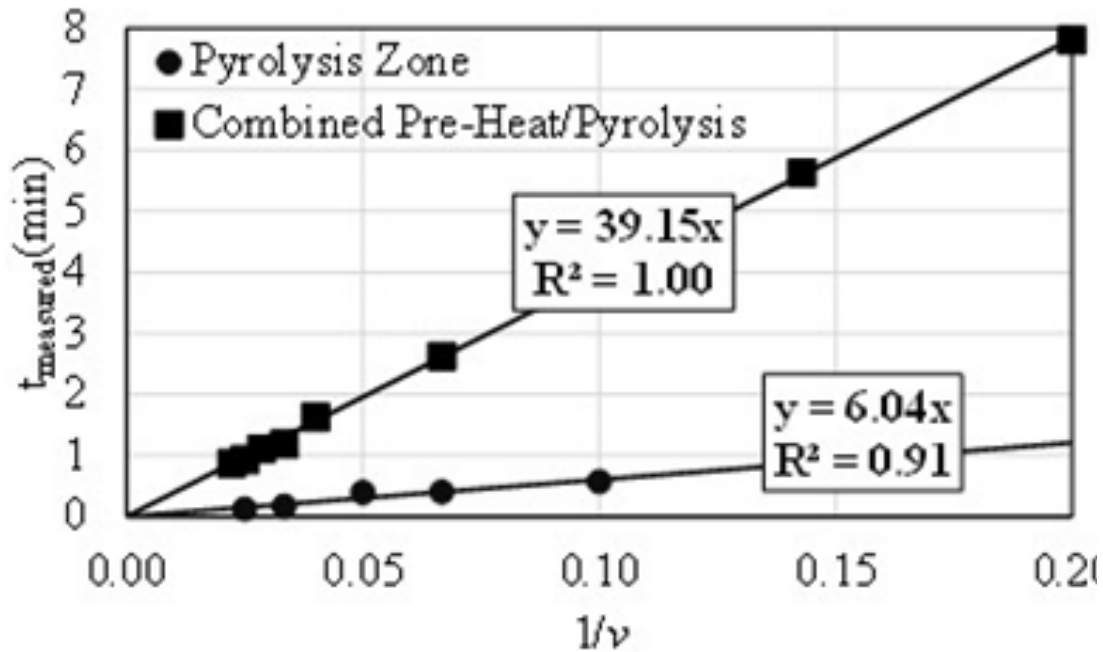


Figure 3-14-Residence time in the reactor.

itches assuming it to be just a normal screw auger. So, the residence time in the reactor at 50 rpm is 32.62 s total and in the pyrolysis zone is 5.03 s and in the HTM zone is 27.59 s.

After the calibration of biomass and HTM under cold condition, several trial runs were conducted in hot conditions which gave us desired results. The rpm of biomass motor was fixed at 3 rpm, sand at 4 rpm and reactor at 50 rpm.

3.2.4 System Design of Lab Scale Setup and Working

The system design is shown in the figure 3-15 which represents the process flow diagram. There are four main components of the fast pyrolysis unit: 1) HTM feed system 2) Biomass feed system. Both the biomass and HTM are based on auger system. 3) The reactor is divided into two zones, the HTM heating zone and the pyrolysis zone. The HTM heating is very well achieved with the use of well stirred reactor. 4) In the fast pyrolysis reaction zone the heated HTM comes in contact with the input biomass. The most important component is the reactor which is based on two main features: i) Cut flights in the spiral auger and ii) Paddles in between every pitch. This combination gave us a desired mixing result. The components will be discussed in the later sections.

The working of this system is as follows: At the start of the experiment, the HTM and the biomass are loaded in the hoppers and the system is sealed. After the system is inserted with high purity nitrogen gas, the system starts heating and at a present temperature ramp

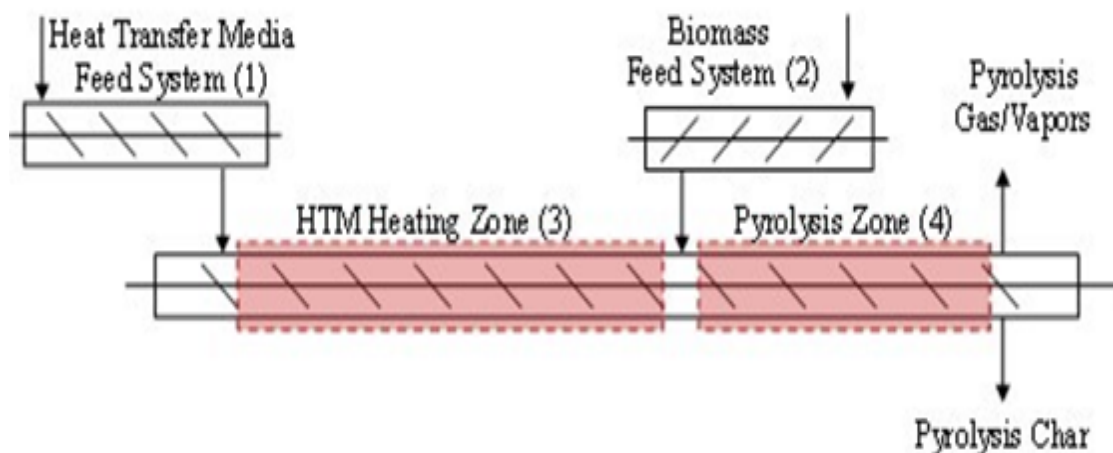


Figure 3-15-Schematic of the process showing major inlet and outlet of the system.

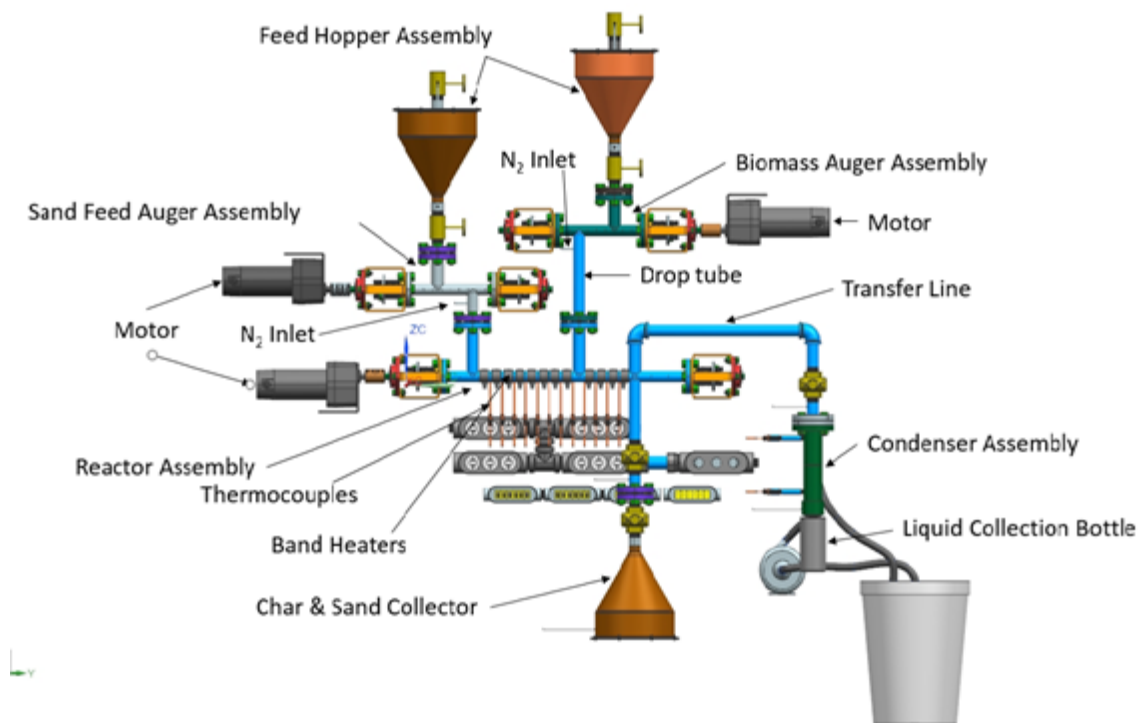


Figure 3-16-Schematic of the fast pyrolysis unit with initial designed hoppers.

until all the heaters have reached steady state. During the system heating, the reactor shaft is rotating so that it also gets uniformly heated. The nitrogen gas also acts as a carrier, and creates a positive pressure gradient through the heat exchanger and to the gas exhaust. Once a steady state is reached, then the HTM feed system is initiated first and as it passes through the HTM preheat zone it starts heating up.

After some time, the HTM reaches the steady state which can be easily inferred from the temperature profile seen in the computer interface and control PID screen. This initial feed of the HTM to re-approach steady state system temperature depends on PID parameters, material flow, etc. but experience has shown it to be approximately 30 minutes. After the HTM has attained its set temperature the biomass feed system is started. The biomass comes in contact with the oncoming HTM in the pyrolysis zone. The vapors formed, travel through the transfer line and the condensable get condensed into the collection bottle after passing through the heat exchanger and the non-condensable exit the system. The char produced, any unreacted biomass and sand are collected in the char collector which is connected at the end of the reactor as shown in figure 3-16. After the experiment is over

the condenser assembly, char & sand collector and condensable bottle are weighed. The product distribution is calculated through gravimetric measurement of the collected product fraction, and weights of the collection equipment by difference.

3.3 Testing Matrix and Procedure

Literature study of numerous research works showed that there are few crucial parameters which have significant effect on bio-oil yield such as reaction temperature, residence time, carrier gas flow rate and biomass particle size. Based on the capability of the system, two parameters, reaction temperature and biomass particle size, were selected for study in this research. Perhaps, the most important parameter is reaction temperature, as it has more influence on maximum bio-oil yield. So, different reaction temperatures were selected in a range from 460°C to 560°C for conducting the experiments.

Another important parameter was biomass particle size. 2 mm is considered as an optimum size for maximizing bio-oil yield [21]. So, three different particle sizes below 2mm were selected for experiments which were size<0.425 mm, 0.425<size<0.850 mm and 0.850<size<1.0 mm. Table 3-1 shows the test matrix for this research.

The plan was to first find the optimum size for max bio-oil yield at a fixed reaction temperature. So, after those experiments we would be having a particular size for maximum bio-oil yield then, that particular size will be fixed and the reaction temperature would be varied to find out optimal temperature for maximum bio-oil yield.

Table 3-1-Test matrix for the experiments of Arundo Donax in the unit.

Experiment #	Size (mm)	Temperature (°C)
1	Size < 0.425	500
2	0.425 < Size < 0.850	500
3	0.850 < Size < 1.0	500
4	0.850 < Size < 1.0	470
5	0.850 < Size < 1.0	530

CHAPTER 4. Results and Discussion

4.1 Introduction

After the experiments were carried out detailed analysis of the data and all the important parameters related to the system were done. The subjects that will be discussed in this section are the characteristics of the novel reactor system, results of the experiments and their interpretation supporting the concepts of mixing quality, heat transfer, residence time, heating rates and the influence of biomass particle size and temperature on bio-oil yield. The thorough literature review discussed above has guided the construction of the experimental test matrix, which gave excellent results, and thus helping in the addition of new knowledge in the field of fast pyrolysis of energy crops in a novel reactor.

4.1.1 Fast Pyrolysis in an Auger Reactor

This section discusses the key performance of the studied auger reactor system.

High Mixing Quality. Technical specifications of the system have been discussed previously in chapter 3. Proper mixing is vital for high heat transfer within the system. Well mixed HTM/biomass ensures that the biomass particles are surrounded with the hot HTM, and the particles go through fast pyrolysis. The combination of cut flights in the auger flighting and four paddles within every pitch has demonstrated high quality mixing. In comparison to a traditional screw, the ratio of effective number of pitches to actual number of pitches was 4.35 due to the modifications. The material requires more revolutions to exit the system because the solid particles are retained through the mixing features. The cut in the auger flighting allows for material to remain stationary instead of be pushed with each revolution, and allows for mixing of material between pitches. The paddles within each pitch act to lift and agitate the material within a pitch, as well as retain material. The effective pitch value shows effective mixing in the small sized reactor. Mixing quality also reflects on the high heating rates and the effective heat transfer between the sand and biomass particles achieved in the system which will be discussed in detail in the following section.

Fast Heating of HTM, Heating Characteristics and Stability. Fast heating rate of the biomass particles is the main factor that defines the fast pyrolysis process and helps in achieving the desired product distribution. Fast heating rate will avoid the development of significant temperature gradient between the biomass particle surface and inside core. Fast heating was done with the help of HTM which provide more surface area to the biomass particles due to its small size and enhances the heat transfer rate as desired. The current system is capable of providing sufficient heat to the HTM in the pre heat zone of the reactor to bring the material to a temperature slightly higher than the desired reaction temperature as described previously. Figure 4-1 represents the temperature dynamics of the reactor.

To prove the heating characteristics and the stability of the system, a trial run was carried out using a 1kg/h and 300 g/h feed rates in the HTM and biomass dosing systems respectively.

This represents a relatively large feedstock loading for the system and was used to demonstrate stability and heating characteristics at the most severe conditions. T1 – T8 represents the temperatures of the preheat section and the T9 – T12 of the pyrolysis zone. The total experiment duration is divided into four main parts as 1) the ramp up time 2) duration of steady state 3) HTM initiated and 4) biomass initiated. Steady operation states (2) are shown at three distinct operation zones: The first occurs after the set temperatures are reached when the system is started.

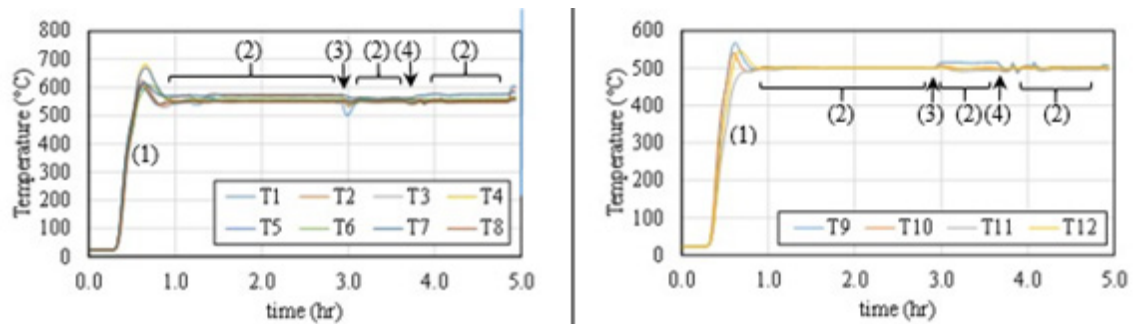


Figure 4-1-Temperature dynamics in the HTM preheat zone(T1-T8) and the reactor(T9-T12) showing: 1) The ramp up time 2) Duration of steady state 3) HTM initiated and 4) Biomass initiated.

The second is after HTM is initiated. The sand draws heat from the surrounding reactor body, and the system re-approaches steady state after the PID heater controllers accommodate the extra heat load. Similarly, the third steady operation state occurs after the biomass dosing is initiated.

From the figure 4-1 it is evident that the system is stable and able to control the fluctuations smoothly when HTM and biomass were added to the system. The temperatures value during these instances are shown in the table 4-1.

The values shown are the average values during a selected interval with \pm one standard deviation. The first time interval was 2.0 to 2.5 h, second was 3.4 to 3.6 h and last one was from 4.6 to 4.8 h (all from the beginning of the startup). It is observed that T2, T6 and T7 are higher than set points and it could be due to close proximity to the heater/thermocouple control loops. The data of temperatures could be strongly supported by the heat duty data of the band heaters as temperature and the duty of heaters are directly related. Figure 4-2 shows the duty curves of the heaters. It is evident from the figure 4-2 that as HTM is initiated at 3 h the duty of the first heater (heater 1, referred to as H1) goes up. H3,4 and 5 also show rise in the duty. H6,7 and 8 show no change in duty, which suggests that they are not supplying power to the HTM as it has already reached the set point temperature.

Table 4-1-Temperature set points and stabilized temperatures at various stages of operation.

	Set point (°C)	Empty System (°C)	With HTM (°C)	HTM and Feed (°C)
T1	550	550.0 \pm 0.1	550.4 \pm 1.0	550.2 \pm 0.9
T2	550	568.4 \pm 0.1	557.3 \pm 0.5	556.5 \pm 0.4
T3	550	550.0 \pm 0.1	550.4 \pm 0.3	550.0 \pm 0.1
T4	550	550.0 \pm 0.2	550.3 \pm 0.4	549.9 \pm 0.2
T5	550	550.0 \pm 0.3	550.3 \pm 0.6	550.0 \pm 0.2
T6	550	558.0 \pm 0.1	555.0 \pm 0.5	558.3 \pm 0.1
T7	550	573.5 \pm 0.1	562.0 \pm 0.4	575.6 \pm 0.1
T8	550	550.0 \pm 0.1	550.3 \pm 0.4	549.9 \pm 1.4
T9	500	500.0 \pm 0.1	514.6 \pm 0.5	500.0 \pm 1.6
T10	500	500.0 \pm 0.1	500.4 \pm 0.3	500.2 \pm 0.5
T11	500	498.6 \pm 0.1	494.2 \pm 0.2	496.5 \pm 0.3
T12	500	500.0 \pm 0.1	500.2 \pm 0.1	500.1 \pm 0.1

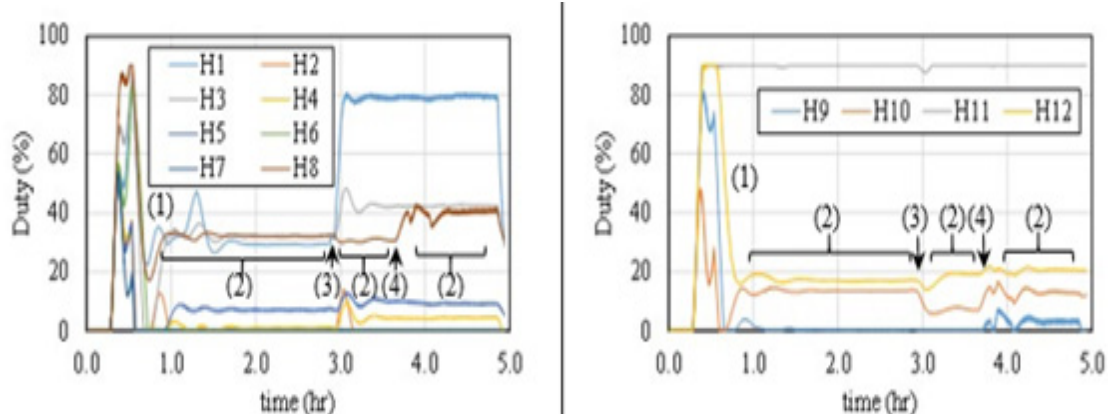


Figure 4-2-Heater duties on the HTM preheat zone(T1-T8) and the reactor(T9-T12) showing: 1) The ramp up time 2) Duration of steady state 3) HTM initiated and 4) Biomass initiated.

It is interesting to note that there is change in the final HTM pre-heat zone heater (H8) as the biomass is initiated. One possible reason is because H8 is near to the incoming flow of the cold biomass, and entering cold stream draws heat from the surrounds, even upstream. This change, however, is minimal and is a less than 9% increase in overall duty cycle from the initial steady state. After the HTM began to flow no change was seen in the duty of the heaters of pyrolysis zone as their set temperature is below the set temperature of the HTM. Table 4-2 represents the averaged duty data of the heaters for the similar time interval as used for the table 4-1.

Table 4-2-Relay duties and stabilized heaters at various stages of operation.

	Empty System (%)	With HTM (%)	Change from Empty System	HTM and Feed (%)	Change from Empty System
H1	29.3±0.1	79.1±0.4	49.8	79.6±0.3	50.3
H2	0.0±0.0	0.0±0.0	0.0	0.0±0.0	0.0
H3	31.8±0.1	42.3±0.3	10.6	42.5±0.1	10.8
H4	0.9±0.1	4.6±0.3	3.6	4.6±0.1	3.6
H5	7.1±0.1	10.4±0.4	3.3	9.2±0.1	2.1
H6	0.0±0.0	0.0±0.0	0.0	0.0±0.0	0.0
H7	0.0±0.0	0.0±0.0	0.0	0.0±0.0	0.0
H8	32.2±0.1	31.1±0.3	-1.1	40.8±0.4	8.6
H9	0.2±0.1	0.0±0.0	-0.2	3.3±0.5	3.1
H10	13.5±0.1	7.5±0.3	-6.0	13.1±0.2	-0.5
H11	90.0±0.0	90.0±0.0	0.0	90.0±0.0	0.0
H12	17.0±0.1	19.2±0.1	2.2	20.7±0.1	3.7

At these levels of loading, a reactor rotation of 50 rpm yielded a residence time of about 47 seconds. The heating dynamics and the time take by the HTM to heat up were calculated by distributing the residence time along the reactor length linearly. The duty values presented in Table 4-2 were then translated through their physical location to an approximate residence time, with time zero as the entrance to the HTM feed. Looking at the table 4-2 and the figure 4-2, the duty cycles after material begins to flow were analyzed with respect to their steady state values. This yields direct insight as to the heat removed at that location in the system, or indirectly, how close the material is to the desired set point temperature. It is important to note that although thermocouples are embedded to approximately measure the material temperature directly at each heater, there are measurement inferences such as the surrounding wall of the reactor, and a small contact area with the HTM/biomass particles that make an average material measurement difficult and the analysis of heater duty more appropriate. We conclude that the change in the duty for the first heater from the initial steady state is about 50%. There is no change in the duty of the second heater and a change of 10% for the third heater and thereon there is no significant change in the duties which clearly defines that the HTM has gained sufficient heat and has reached the set temperature. A first order decay was fit by minimizing the squared difference between data and model, and a characteristic time of about 3 seconds was obtained.

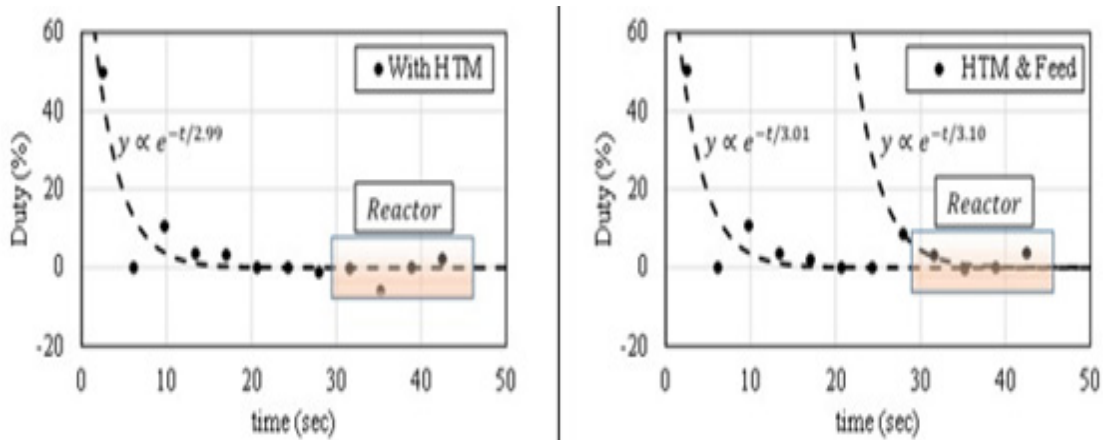


Figure 4-3-Change in heater duties at steady state with flow of HTM (left) and with flow of HTM and feedstock (right) as function of residence time in the system.

In a similar fashion, data were obtained for heaters duty when the HTM and biomass dosing systems were both active. As discussed before, the final heater in the pre-heat zone (H8) also plays a role in heating the cold biomass due to its close proximity to the biomass inlet drop tube, and can also be seen from its increase in the duty value when biomass starts flowing. It was therefore included in determining the heating characteristics of the biomass. The figure 4-3 and table 4-2 suggests that the change in the duty in the reactor zone was very little, which signifies that most of the heat was provided by the heated HTM and the material was heated to the desired temperature on average. This demonstrates our goal of transferring most of the heat from the HTM. The characteristic time obtained was also about 3 seconds and proves low heating time in strong support that fast pyrolysis occurs in our novel reactor, and good mixing indirectly. A potential future refinement to this measurement would require additional band heaters/thermocouples to have better time resolution, or to use a faster RPM to artificially enhance the time-resolution. It was only studied at 50 RPM here to ensure analysis at experimental conditions and did not incorporate mixing effects that would not typically be observed. It is important to note, again, that this study of heating load of HTM and biomass was high (3.3 HTM : 1 biomass). In production runs a more typical value is between 10:1 and 20:1 (as discussed in the review previously for auger and fluidized beds). These experiments were designed to exaggerate the effects of the heating delay between a low amount of HTM relative to the biomass. With proper ratios of HTM and biomass it is likely much faster heating can be achieved due to more available heated contact area, and these results will hold strongly. During experimental trials with typical HTM ratios, heaters showed very little or no increase throughout the reactor zone.

Inert Gas. Another advantage is very little use of inert gas as compared to the fluidized bed which can possess high cost. The biomass flow rate was approximately 100g/h. The average nitrogen flow rate during experiments was 0.5 SCFH which is equivalent to 0.235 L/min. This value is very low (~1%) compared to fluidized bed which is typically 20 L/min. So, the inert gas consumption can be represented as to process 100 g of biomass requires 14.1 L/h as compared to fluidized bed. During the startup high nitrogen flow is set to purge

the system and to seal the leaks in the system. During running condition, the flow rate is reduced to around 0.5 SCFH sufficient enough to prevent back flow of the pyrolysis vapors and help the vapors to reach the condenser via convection. So the low use of inert gas would prove vital for scaling up of the system as fluidized is not needed and hence the system size would also not be huge.

4.2 Effect of Different Parameters On Bio-Oil Yield

As discussed through the thesis we assert that there are many crucial parameters influencing the bio-oil yield such as reaction temperature, biomass particle size, type of reactor used, use of HTM, flow of inert gas and condensing system. Based on the literature study, two parameters were selected (reaction temperature and biomass particle size) for the experimental investigation. Results are discussed in the following subsections.

4.2.1 Effect of Biomass Particle Size On Bio-Oil Yield

The study of the particle size is important as it gives the information on the heat and mass transport phenomena impacts, and effects of constituents that may vary based on size (or size exclusion) such as mineral content (and therefore percentage volatile matter etc.) and carbohydrate/fiber distributions. These effects are interpreted through the bio-oil yield in the current auger system. Numerous studies typically used small sized biomass fraction around 2 mm for fast pyrolysis.

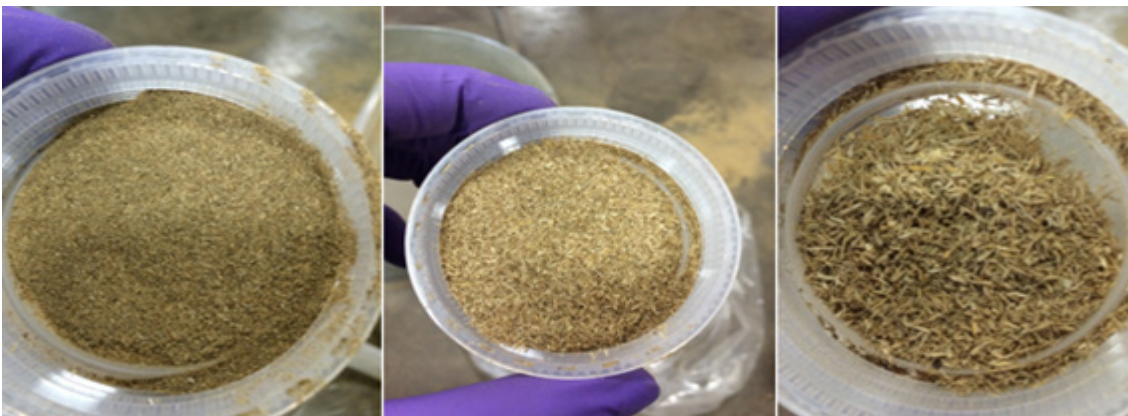


Figure 4-4-(Starting from left to right)- Arundo Donax size $<0.425\text{mm}$, $0.425 < \text{size} < 0.850\text{mm}$ and $0.850 < \text{size} < 1.0\text{ mm}$.

Initially 6 different size ranges were sorted out, which were < 0.425 mm, $0.425 < \text{size} < 0.850$ mm, $0.850 < \text{size} < 1.0$ mm, $1.0 < \text{size} < 2.0$ mm, $2.0 < \text{size} < 3.3$ mm and > 3.3 mm. Different sieve sizes which were 3.3mm, 2mm, 1mm, 0.850mm and 0.425mm from this manufacturer were used. The approximate shaking time was about 30s. Due to the plugging of biomass with the small and compact design of the system the three size ranges were selected for study which are < 0.425 mm, $0.425 < \text{size} < 0.850$ mm and $0.850 < \text{size} < 1.0$ mm as shown in the figure 4-4. It was observed that our ground biomass possessed high length to diameter ratio so it was sieved below 1 mm fractions. It is important to note that the diameter of the particles is not related to the length of the particles.

The purpose for performing these set of experiments was to find out the size which produces maximum bio-oil at a particular temperature (500°C) and then at that particular size the variation of temperature could be studied. Figure 4-5 shows condensable vs size results. Figure 4-7 shows the bar graph of condensable as is basis and the figure 4-5 shows the dry ash free (d.a.f) basis. It is clearly seen that the maximum bio-oil yield is at the middle size fraction. The smallest size fraction gives the lowest bio-oil yield which may be due to the large amount of minerals present in it ($\sim 15\%$). Ash is mostly composed of alkali

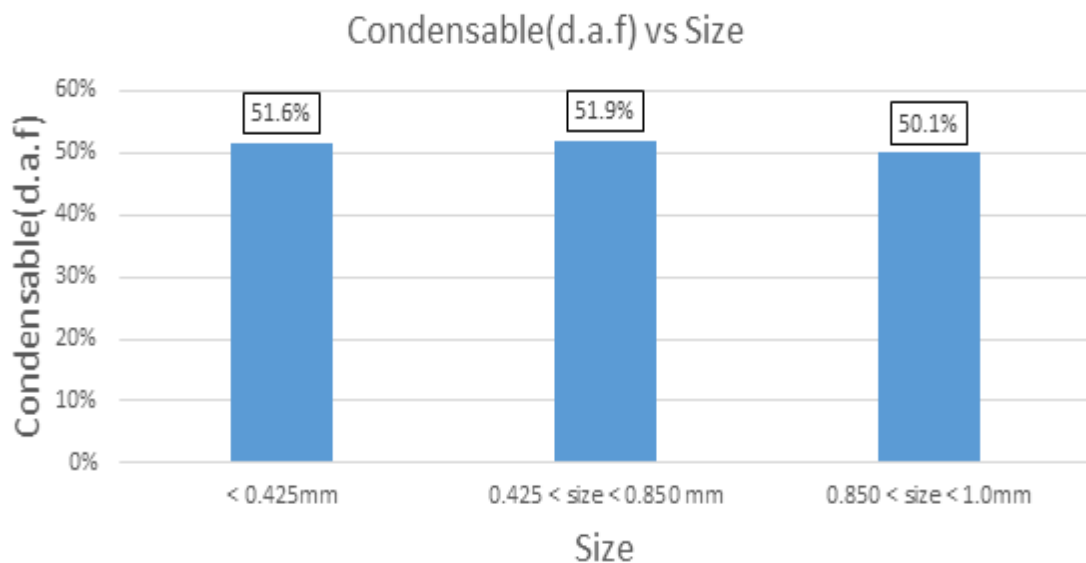


Figure 4-5-Condensable yield (d.a.f) for different biomass particles size.

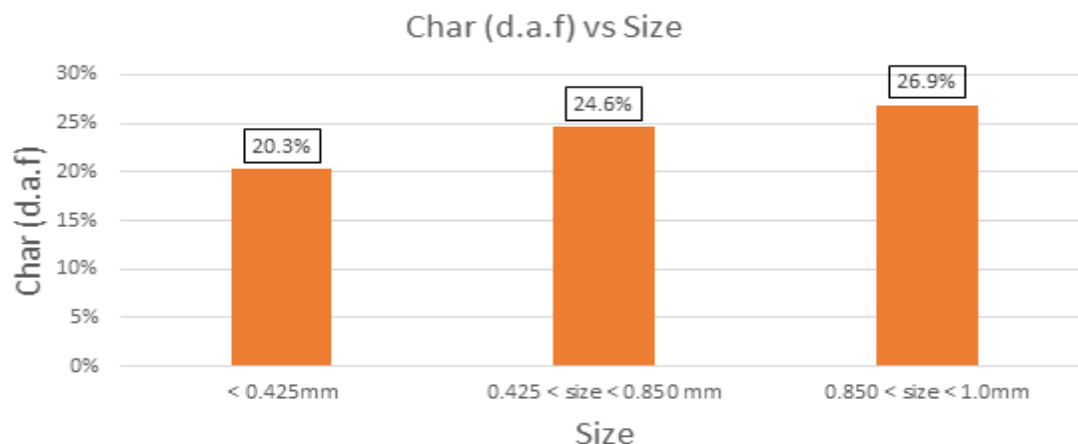


Figure 4-6-Char yield (d.a.f) for different biomass particles size.

and alkali earth metals which catalyze secondary reactions such as vapor phase cracking and repolymerization to produce more char and non-condensable pyrolysis gases [16]. Minerals content of ash of arundo donax can be found in appendix B, table B-1. Interestingly, the formed char (ash-free) is lowest for this particle size as well. This may suggest that these alkali metals aid in converting the more recalcitrant char/carbon structures to volatile components. This effect may be convolved with slight impact of large particles resulting in slightly unreacted biomass. The large particle size gave a little less (less by 1% than maximum yield) yield of condensable liquids which is likely not significant, and these values are approximately equal.

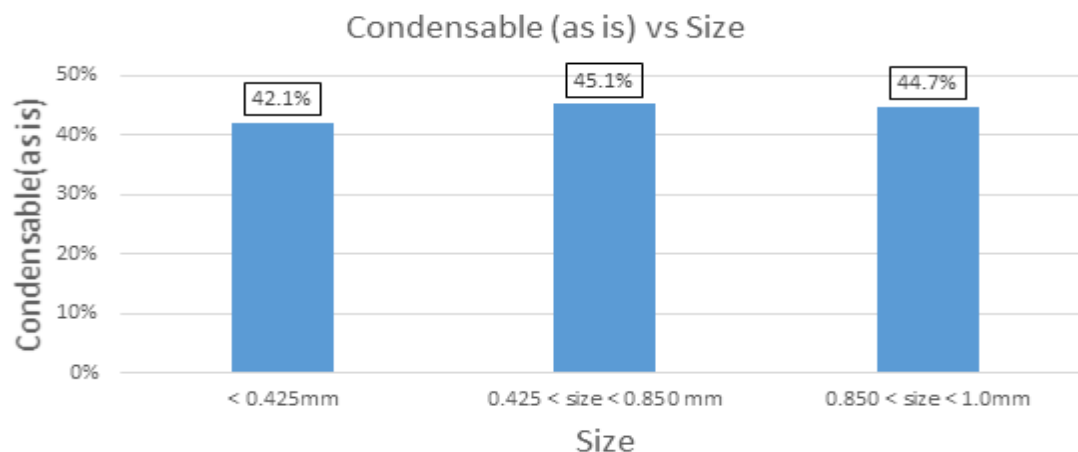


Figure 4-7-Condensable yield (as is) for different biomass particles size.

Based on figure 4-5 it can be said that condensable (d.a.f) gave almost same bio-oil yield signifying that there is no substantial effect of different sizes on the bio-oil yields if minerals are not considered in the initial mass, or that if only the convertible mass is considered they have similar yields. Further, it can be concluded that all the three particle size possess sufficient surface area compared to the particle diameter for the effective heat transfer to occur and avoid temperature gradient within the biomass particles. This agrees with typical literature values that particles must be less than 1-2mm to avoid significant gradient effects.

Table 4-3 presents the data of the condensable based on as-is basis and dry ash free basis. As we can see that the percentage of ash drastically reduces with increasing size. It means that all the minerals are small in size which got sieved with the smallest size of biomass fraction. This could be because this is an agricultural energy crop and it could contain lot of alkali and alkali earth metals so a simple pretreatment method such as water washing may remove significant metals which could increase the bio-oil yield. The ash content decreased by 34.21 % from lowest size to the middle size which resulted in an increase of 7% in bio-oil yield. Also, for the smallest fraction there is an increase of 22.56% in bio-oil yields compared to dry ash free basis. So removal of minerals is very important to obtain high bio-oil yields from energy crops. Figure 4-6 shows that the char yield (d.a.f basis) increases with increasing size which is according to the expected trend. There is an increase of 32.51% from the smallest to the highest size fraction.

Table 4-3-Measurements of the Biomass fed and products obtained for different sizes.

Size	As-is basis					Dry, ash free		
	Mass fed (g)	Condensable (%)	Char (%)	Moisture (%)	Ash (%)	Mass fed (g)	Char (%)	Condensable (%)
< 0.425mm	402	42.1	31.2	3.8	15.2	328	20.3	51.6
0.425 < size < 0.850 mm	401	45.1	31.0	3.5	10.0	348	24.6	51.9
0.850 < size < 1.0mm	403	44.7	31.1	3.7	7.4	360	26.9	50.1

4.2.1 Effect of Reaction Temperature On Bio-Oil Yield

The main operational parameter of fast pyrolysis is temperature which highly influences the bio-oil yield. The main components of energy crops are cellulose, hemicellulose and lignin which decomposes in sequence as the temperature rises. Breaking of large heavy molecules take place at elevated temperature range of 400-550°C for mainly bio-oil production. The important task is to find out an optimal temperature for maximum bio-oil yield for arundo donax. So, after the size was fixed three different values of temperature were decided to carry out experiments which were decided based on literature study. Figure 4-8 clearly proves our all previous assumptions of the trend that was to be expected. These results show that yield of bio-oil for arundo donax at 500°C is almost the same at 470°C. So, for arundo donax the optimal temperature likely has an optimum range (470-500°C) in which maximum bio-oil yield can be obtained. As we go higher with temperature from 500°C the bio-oil yield decreases and at 530°C the yield decreased by 7.0%. There is a clear trend of parabolic shape as we increase the temperature from 470 to 530°C and at the tip we get optimal values of temperatures for maximum bio-oil yield. This trend is consistent with other herbaceous feedstock and energy crops [33].

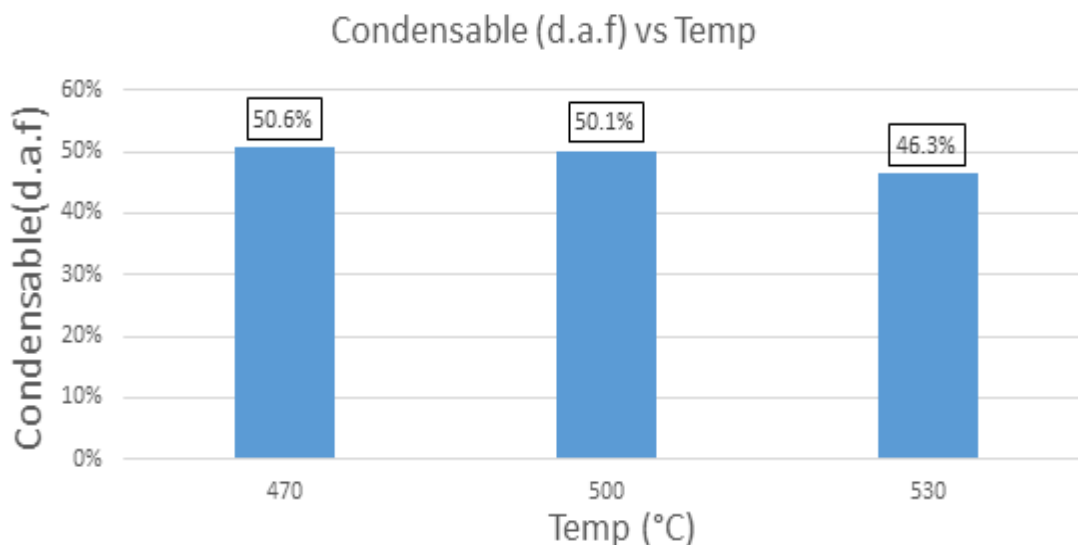


Figure 4-8-Condensable yield (d.a.f) for different reaction temperatures.

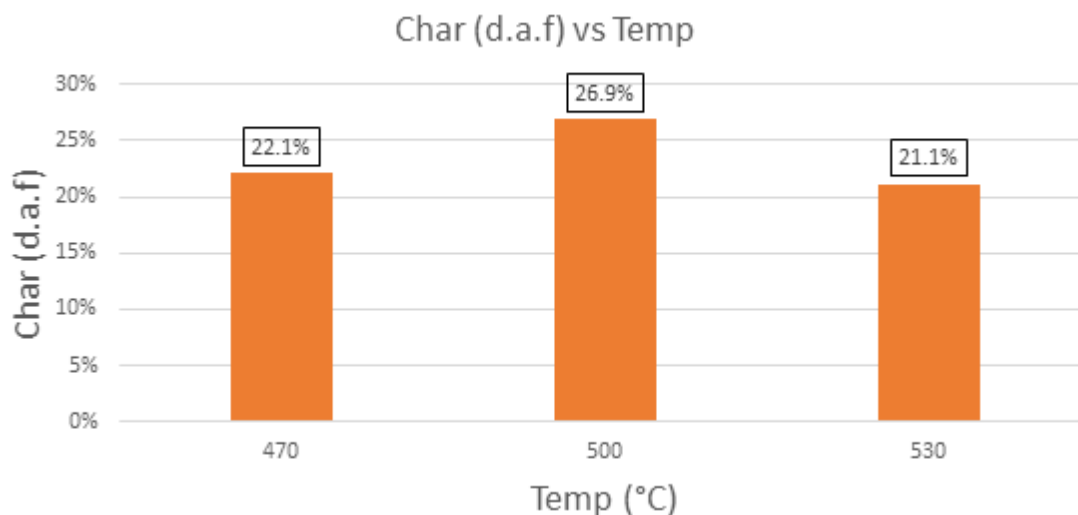


Figure 4-9-Char yields (d.a.f) for different reaction temperatures.

In general, these materials tend to have a high ash (alkali metal) content. In addition to the balance between temperature and secondary thermal reactions, such materials also have secondary reaction with respect to the alkali metals that must be balanced.

As a result, the maximum oil production is typically found at a lower temperature. This sufficiently degrades the structure while not promoting the catalytic cracking reactions that dominate at relatively higher temperature conditions. In addition, herbaceous materials and energy crops tend to have lower lignin content than wood feedstock and do not require such high temperatures to fully degrade the biomass constituents. The char yield is not affected by the change in temperature as seen in figure 4-9.

Prior to using arundo donax, this system was rigorously tested with different feedstocks to prove the feasibility of the technology and the system. Repeated tests with other feedstocks has shown the oil is repeatable to 2-3% (from the mass of feed). Moreover, the qualitative agreement between results obtained from the system at MTU and the fluidized bed system (NREL) yield validity of results with other fast pyrolysis systems. After the reactor validation Arundo donax was used to investigate in our system and the results are believed to be repeatable. Refer appendix A for more details which includes the type of feedstocks used and figure showing comparable results of MTU and NREL (National Renewable Energy Laboratory) system.

CHAPTER 5. Conclusions

5.1 Conclusion

A working lab-scale novel paddle reactor was designed, constructed, researched and demonstrated for biomass fast pyrolysis. The objective of this research attempt was to demonstrate the effectivity of a novel paddle reactor for fast pyrolysis and to see the effect of Arundo Donax, mainly the effect of biomass particle size and reaction temperature, on the bio-oil yield. As this is an emerging technology there are relatively few published materials that cover fast pyrolysis in auger reactors, or the fast pyrolysis of Arundo Donax. This study contributes to both pools of knowledge.

Literature review specifically focusing on the auger technology was presented in chapter 2. A focused literature review covered auger reactors, auger reactors for fast pyrolysis, and investigated the various capacities across various research groups and presented a consolidated summary. Many different parameters are involved in the characterization of the fast pyrolysis, and it was concluded that due to the volatile nature of fast pyrolysis it is difficult to predetermine a set of parameters to obtain desired product distribution at various reactor scales. As many feedstock and technology parameters influence the outcomes of pyrolysis, an empirical study was designed to investigate the conversion of an emerging energy crop with a novel configuration of the auger reactor.

Chapter 3 was focused on the development of the fast pyrolysis unit and to demonstrate a specific characteristic: mixing quality of the system. The mixing quality was proved with help of the concept of effective number of pitches and in the following section through the analysis of heating time. The novel paddle reactor has cut flights and paddles generating inefficiency in conveying the material. The cut flights allow mixing between auger pitches and the paddles within each pitch enhance mixing between each pitch. Also, the experimental setup, components and the working of the unit is explained in detail.

Chapter 4 discussed the results of the heating characteristics and stability of the system. The temperatures of the reactor and the data of the duty cycle from the PID was used to develop the correlations for the heating characteristics and the characteristic heating time

of approximately 3 s was determined. The use of sand as HTM enhanced the heat transfer rate by having more surface area exposed to the biomass particles rather than a simple heated reactor walls. The effect of the size of biomass particles of *Arundo Donax* and reaction temperature on the bio-oil yield is discussed in detail. It was concluded that the effect of biomass particle size on the bio-oil yield is not significant for *Arundo Donax* while the effect was observed in the char yield which was seen to be strictly increasing with the increasing biomass particle size. There was an increase of 32.5% in char yield with the increase in particle size from the smallest 425 μ m to the highest fraction 850<size<1000 μ m. The effect of reaction temperature was seen as expected. A slight parabolic curve was obtained as the reaction temperature was varied from 470 to 530°C and the highest bio-oil yield about 50% was obtained in the range of 470-500°C for *Arundo Donax*. Reduction of about 7% was observed at 530°C compared from 500°C. Typically, for energy crops the highest bio-oil yields are obtained at temperatures lower than 500°C as compared to woody biomass which give highest bio-oil yield at approximately 500°C. The effect of reaction temperature on the char yield was not significant and was not pursued further.

5.2 Future Work

This system is very well suited for testing different types of feedstocks giving high quality bio-oil. But there are few improvements to be done in the system. As discussed in section 3.2.1 the biomass and HTM feeding hoppers were modified and their auger conveying system so a better agitator could be used which can prevent the bridging to significant extent and avoid the plugging of the material in the feeding augers and the drop tubes due to the interlocking and complex structure of biomass. Another area of improvement is in the nitrogen inputs. Currently we used nitrogen flow at two inlets, each at the both feeding drop tubes but few more connection are required, one at the hoppers and one at the bottom of the drop tubes which will create curtain and prevent the flow of vapors and the wetting of HTM material. Use of sand as HTM has eroded material from the reactor shaft which will create problems in the conveying of the material if used extensively so, less abrasive HTM should be used. Replacement of char could be done as the hardness of char is 0.5-1

as compared to 7 for sand. Moreover, the conductivity of char is 1.7 W/m-K which is almost double than sand 0.71 W/m-K.

Keeping in mind the results, conclusions and the scope for future work we have proposed a potential scale-up of the system. The current system had a 1" auger housing and we have already procured 4" system for further investigation.

More and more efforts are put today in the area of renewable energy but it is very important that along with solving technical challenges associated we need to focus on the social and the economic viability of these processes.

Works Cited

- [1] L. E. Doman, V. Arora, L. E. Singer and M. Lynes, "International Energy Outlook, 2016," EIA, Washington, 2016.
- [2] R. Brown, *Biorenewable Resources: Engineering New Products from Agriculture.*, Ames, IA: Blackwell Publishing, 2003.
- [3] P. McKendry, "Energy production from biomass (part 2): conversion technologies," *Bioresource Technology*, vol. 83, pp. 47-54, 2002.
- [4] R. Broek, A. Faaij and A. Wijk, "Biomass combustion for power generation," *Biomass and Bioenergy*, vol. 11, no. 4, pp. 271-281, 1996.
- [5] A. Demirbas, "Biomass resource facilities and biomass conversion processing for fuels and chemicals," *Energy Conversion and Management*, vol. 42, pp. 1357-1378, 2001.
- [6] M. Ringer, V. Putsche and J. Scahill, "Large-scale pyrolysis oil production: A technology Assessment and Economic Analysis," National Renewable Energy Laboratory, Colorado, 2006.
- [7] F. Bilgili and I. Ozturk, "Biomass energy and economic growth nexus in G7 countries: Evidence from dynamic panel data," *Renewable and Sustainable Energy Reviews*, Vols. 132-138, p. 49, 2015.
- [8] S. Czernik and A. Bridgwater, "Overview of Applications of Biomass Fast Pyrolysis Oil," *Energy & Fuels*, vol. 18, no. 2, pp. 590-598, 2004.
- [9] D. Meier and O. Faix, "State of the art of applied fast pyrolysis of lignocellulosic materials-a review," *Bioresource Technology*, vol. 68, no. 1, pp. 71-77, 1999.

- [10] A. Demirbas, "The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis," *Fuel Processing Technology*, vol. 88, no. 6, pp. 591-597, 2007.
- [11] A. Bridgwater, D. Meier and D. Radlein, "An overview of fast pyrolysis of biomass," *Organic Chemistry*, vol. 30, no. 12, pp. 1479-1493, 1999.
- [12] A. Demirbas, "Progress and recent trends in biofuels," *Progress in Energy and Combustion Science*, vol. 33, no. 1, pp. 1-18, 2007.
- [13] R. Venderbosch and W. Prins, "Fast pyrolysis technology development," *Biofuels, bioproducts and biorefining*, vol. 4, no. 2, pp. 178-208, 2010.
- [14] A. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and bioenergy*, no. 38, pp. 68-94, 2012.
- [15] B. Wagenaar, J. Kuipers, W. Prins and W. Van Swaaij, "The Rotating Cone Flash Pyrolysis Reactor," University of Twente, Netherlands.
- [16] S. Sirijanusorn, K. Sriprateep and A. Pattiya, "Pyrolysis of cassava rhizome in a counter-rotating twin screw reactor unit," *Bioresource technology*, vol. 139, pp. 343-348, 2013.
- [17] S.-S. Liaw, S. Zhou, H. Wu and M. Garcia-Perez, "Effect of pyrolysis temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas Fir wood.," *Journal of Analytical and Applied Pyrolysis*, no. 93, pp. 52-62, 2012.
- [18] A. Veses and et al., "Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts.," *Bioresource technology* 162 (2014): 250-258., no. 162, pp. 250-258, 2014.
- [19] R. Brown and J. Holmgren, "Fast pyrolysis and bio-oil upgrading.," *Gas*, vol. 13, p. 25, 2009.

- [20] C. E. Efika, C. Wu and P. T. Williams, "Syngas production from pyrolysis–catalytic steam reforming of waste biomass in a continuous screw kiln reactor.," *Journal of Analytical and Applied Pyrolysis*, vol. 95, pp. 87-94, 2012.
- [21] J. N. Brown, "Development of a lab-scale auger reactor for biomass fast pyrolysis and process optimization using response surface methodology," Iowa State University, 2009.
- [22] C. U. e. a. Pittman Jr, "Characterization of bio-oils produced from fast pyrolysis of corn stalks in an auger reactor.," *Energy & Fuels*, vol. 26, pp. 3816-3825, 2012.
- [23] S. Kelkar, C. M. Saffron, L. Chai, J. Bovee, T. R. Stuecken, M. Garedew, Z. Li and R. M. Kriegel, "Pyrolysis of spent coffee grounds using a screw-conveyor reactor.," *Fuel Processing Technology*, vol. 137, pp. 170-178, 2015.
- [24] N. Puy, R. Murillo, M. V. Navarro, J. M. Lopez, J. Rieradevall, G. Fowler, I. Aranguren, T. Garcia, J. Bartroli and A. M. Mastral, ""Valorisation of forestry waste by pyrolysis in an auger reactor.," *Waste management*, vol. 31, pp. 1339-1349, 2011.
- [25] J. D. S. a. J. D. Haydary, "Pyrolysis of aseptic packages (tetrapak) in a laboratory screw type reactor and secondary thermal/catalytic tar decomposition.," *Waste management*, vol. 33, pp. 1136-1141, 2013.
- [26] Y. C. a. Y. N. P. Chen, "Effects of Grain Size and Rotational Speed on the Bio-Oil Yield in a Fast Pyrolysis Reactor Employing a Single Tapered Screw Extruder.," *Advanced Materials Research*, vol. 347, 2012.
- [27] J. Haydary, D. Susa, V. Gelinger and F. Cacho, "Pyrolysis of automobile shredder residue in a laboratory scale screw type reactor.," *Journal of Environmental Chemical Engineering*, vol. 4, pp. 965-972, 2016.

- [28] M. Day, J. D. Cooney and Z. Shen, "Pyrolysis of automobile shredder residue: an analysis of the products of a commercial screw kiln process," *Journal of analytical and applied pyrolysis*, vol. 37, pp. 49-67, 1996.
- [29] M. Day, Z. Shen and J. D. Cooney, "Pyrolysis of auto shredder residue: experiments with a laboratory screw kiln reactor," *Journal of Analytical and Applied Pyrolysis*, vol. 51, pp. 181-200, 1999.
- [30] L. Ingram, D. Mohan, M. Bricka, P. Steele, D. Strobel, D. Crocker, B. Mitchell, J. Mohammad, K. Cantrell and C. U. J. Pittmann, "Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils," *Energy & Fuels*, vol. 22, pp. 614-625, 2008.
- [31] L. Bosong, L. Wei, Z. Qi, W. Tiejun and M. Longlong, "Pyrolysis and catalytic upgrading of pine wood in a combination of auger reactor and fixed bed.," *Fuel*, vol. 129, pp. 61-67, 2014.
- [32] E. Henrich, N. Dahmen, F. Weirich, R. Reimert and C. Kornmayer, "Fast pyrolysis of lignocellulosics in a twin screw mixer reactor," *Fuel Processing Technology*, vol. 143, pp. 151-161, 2016.
- [33] A. A. B. Charles A. Mullen, "Fast Pyrolysis and Bio-oil Production from Agricultural Residues and Energy Crops," [Online]. Available: www.ars.usda.gov/naa/errc.

Appendix A: Experiments and Technology Feasibility

Prior to performing the experiments with Arundo Donax, a number of different feedstock types were tested to prove the feasibility of the fast pyrolysis paddle technology shown in Figure 3-1 and described in Chapter 3 of the main text. Feedstocks tested included woody, herbaceous, agricultural residues, energy crops, and a blend of materials. A primary set of tests is shown in Table A-1 and several feedstocks were tested in duplicate.

Table A-1-Different feedstocks tested.

1	Switchgrass (SG)
2	Corn Stover
3	Corn Stover
4	Clean Pine (CP)
5	Torrefied Pine (TP)
6	Blend (CP, TP, SG)
7	Pinion-Juniper
8	Tulip Poplar (TP)
9	Hybrid Poplar
10	Construction and Demolition Waste
11	Miscanthus
12	Miscanthus

The results from screening of these materials was then compared to runs completed in the National Renewable Energy Laboratory's (NREL) two-inch circulating fluidized bed reactor (2FBR). It is important to note that the materials tested were from the same bulk material samples, and should have very similar physio-chemical composition, making a direct comparison more applicable. Figure A-1 below show the results of a fluidized bed and the novel paddle reactor (mixing auger) with using sand (HTM). When sand is used as HTM then results comparable to fluidized system are obtained as can be seen in figure A-1. While the results are not described quantitatively here, the qualitative agreement between results obtained from the system at MTU and the fluidized bed system yield validity of results with other fast pyrolysis systems. It is important to note that replicate tests with these feedstocks yielded similar liquid product yields, and were within

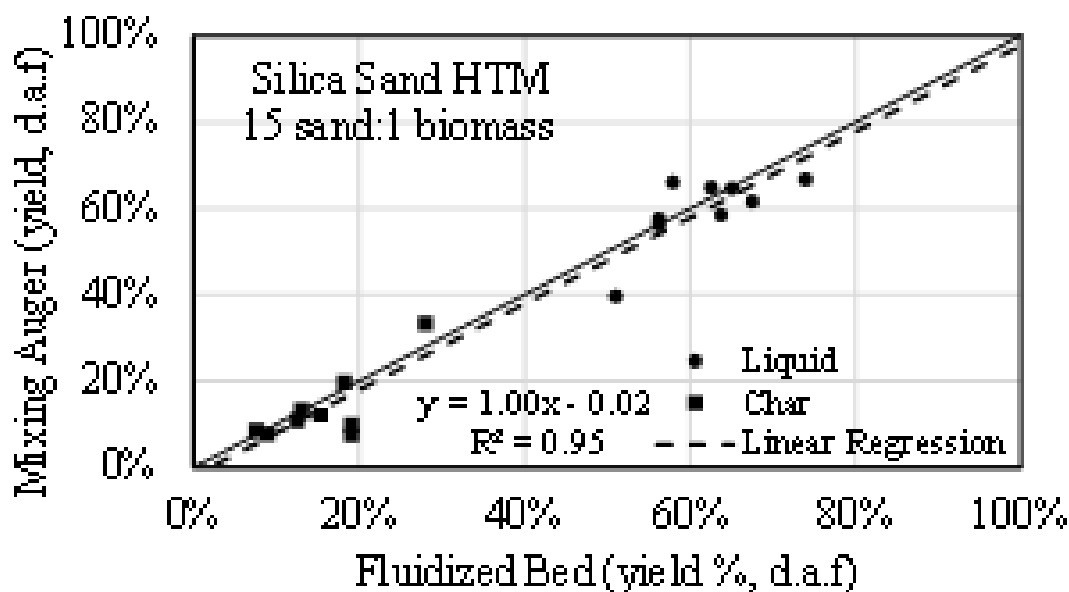


Figure A-1-Comparison of fluidized bed reactor and novel paddle reactor with using sand as HTM.

approximately 2% yield (these data are difficult to distinguish from Figure A-1 as the data points nearly line up). After this set of experiments, the reactor was considered validated and tests were performed with Arundo Donax.

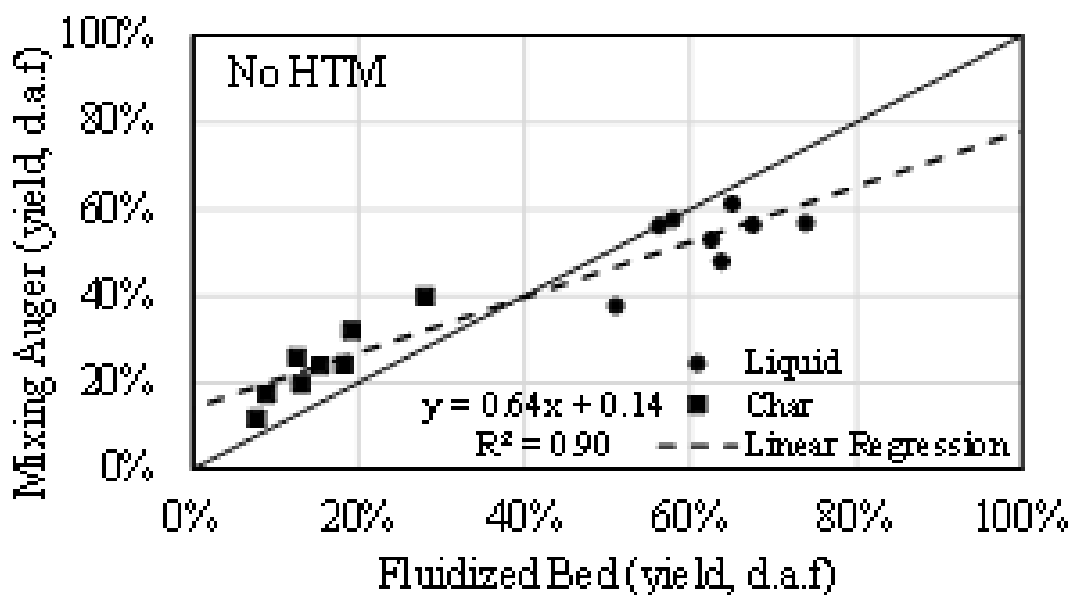


Figure A-2-Comparison of fluidized bed reactor and novel paddle reactor without using sand as HTM.

Figure A-2 compares the results of fluidized bed and the novel paddle reactor (mixing auger) without using sand as HTM. The results from the mixing auger are not in complete agreement showing variations which suggests that importance of using sand as HTM to obtain comparable results to fluidized bed as seen in figure A-1.

Appendix B: Instruments used Equipment

A number of commercially available equipment was used in preparation of the Arundo Donax prior to testing in the fast pyrolysis reactor, and testing of the raw material. The following figures are primarily in support of Section 3.2.2 of the main text. As the procedures are described in the main body of the text and the products are commercially available, a detailed discussion is not provided here.

Figure B-1 shows the high speed rotor grinder that was used in size reduction of Arundo Donax. Material was charged into the batch grinder, and processed for a pre-determined set of time (approximately 30 seconds) to yield a desired range of particle sizes.



Figure B-1-Laboratory high-speed rotor mill/grinder.

After grinding the materials was sieved to different particle sizes of interest. ASTM specification analytical sieves were used, as shown in Figure B-2.



Figure B-2-0.850 and 0.425 mm sieves.

Material drying was performed in a batch laboratory convection oven at 120°C. Drying was performed until the material reached approximately less than 10% moisture.



Figure B-3- Convection Oven.

A Thermo Scientific muffle furnace was used to ash biomass samples. Samples were ashed at 575°C to a constant weight.



Figure B-4-Muffle furnace.

An OHAUS moisture analyzer was used to determine moisture content of biomass samples. A factory preset program measure change in mass of the sample while heating to a preset temperature (120°C) until a change is no longer detected. The moisture measurements were also compared again by manual gravimetric tests with the drying over, and were found to give identical results.



Figure B-5-Moisture analyzer.

Table B-1 includes the ash analysis of arundo donax. Minerals such as Si and K are present in large amount in the feedstock.

Table B-1-Arundo donax ash analysis.

Minerals	Chemical formula	As received (%)
Silica	SiO ₂	47.34
Alumina	Al ₂ O ₃	2.91
Titania	TiO ₂	0.25
Lime	CaO	6.00
Ferric Oxide	Fe ₂ O ₃	4.06
Potassium Oxide	K ₂ O	25.53
Magnesium Oxide	MgO	2.29
Sodium Oxide	Na ₂ O	1.78
Sulfur Trioxide	SO ₃	2.76
Phosphorus Pentoxide	P ₂ O ₅	1.88
Barium Oxide	BaO	0.05
Manganese Dioxide	MnO ₂	0.09
Strontium Oxide	SrO	0.03
	Undetermined	5.03

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