Biomass Pyrolysis

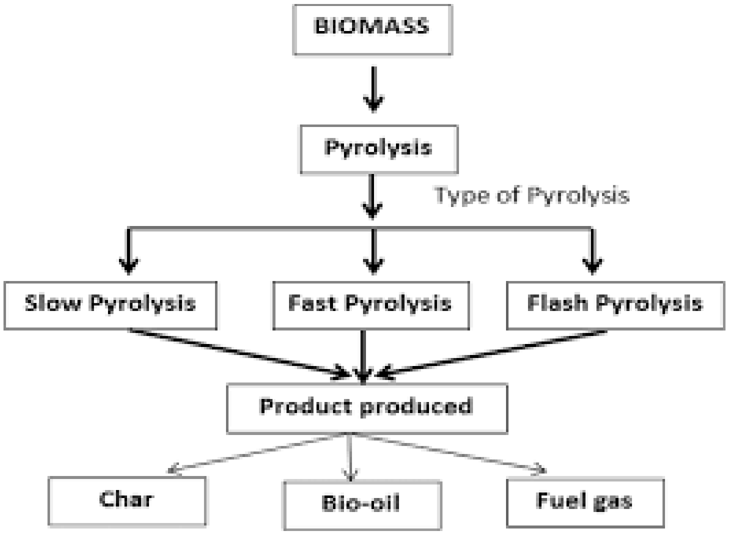
* Definition of Pyrolysis

- pyrolysis is the combination of two Greek words, 'pyro' means 'fire' and 'lysis' means 'separating' i.e. separation by fire or heat.
- it is also called 'thermolysis'.
- Encyclopedia Britannica
  - it is the chemical decomposition of organic (carbon-based) materials through application of heat in the absence of oxygen.
  - in the first step gasification and combustion occur in the absence or near absence of oxygen
  - it is different from combustion which takes place only if sufficient oxygen is present
  - rate of pyrolysis increases with temperature
  - industrial application — temperatures used are often ~~430°c~~ 430°c or higher
  - two well known products — charcoal or biochar created by reacting wood (biomass), coke created by heating coal.
  - also produces condensible liquids (or tar) and non-condensible gases

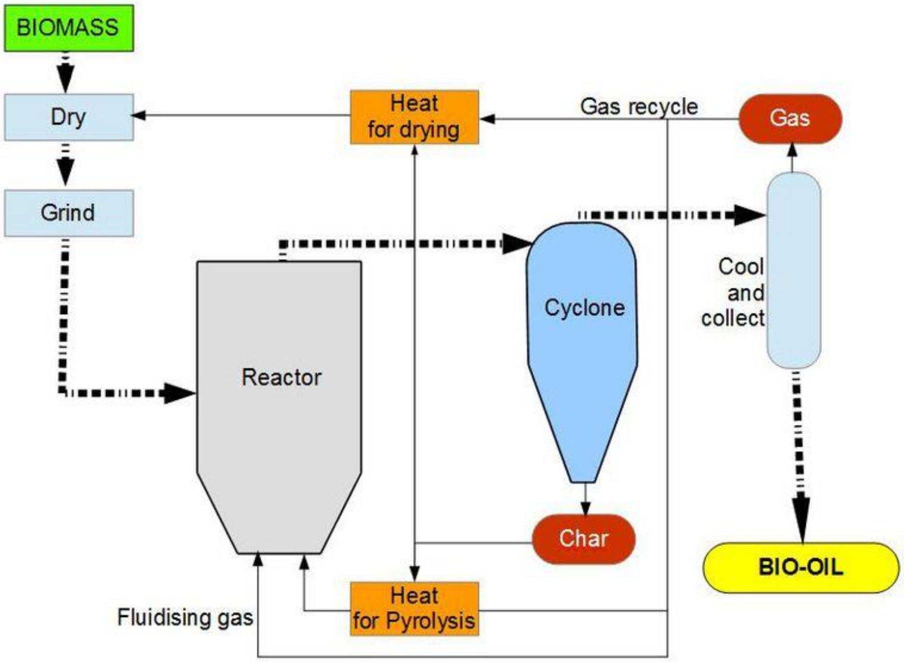
* Biomass Pyrolysis (Figure 3-1)

- biomass profusely available everywhere is an important renewable energy source
- it is an alternative to partially or replace the fossil fuels and nuclear energy
- 50% of global population depends on biomass for energy
- technological developments in recent years allow the biomass to be used as energy source with low levels of emissions and environmental impacts
- biomass is converted into energy by various technologies
- among all conversion techniques of biomass, plyrolysis offers number of benifits:

Biomass Pyrolysis



(a)



(b)

Figures-1 (a, b): The process of pyrolysis.

③

- less emissions of pollutants and the flue gas
- gives solid (biochar), liquid (bio-oil) and gaseous (biogas) products
- all by-products can be re-used
- bio-oil obtained in pyrolysis has advantage over petroleum product due to renewable nature
- bio-oil can be used for further production of many chemicals

- biomass pyrolysis process is carried out in three stages:
  - dosing and feeding of the raw materials
  - transformation of the organic mass
  - separation of the products
- distribution of ~~produs~~ products is effected by:
  - heating rate
  - final temperature, and
  - pressure
  - Residence time
- the products of biomass pyrolysis include bio-char, bio-oil and gases (biogases) containing CH_4, H_2, CO, CO_2 depending on temperature, heating rate, residence time

process variants with main products are given in the Table-1

Process	Temp (°C)	Heating Rate	Residence Time	Products
Fast	650	Very High	0.5-5 sec.	Bio-oil
Conventional (Slow Pyrolysis)	600	Low	15-30 min	Oil, gas, char
Carbonization	400	Very low	Days	Charcoal
Ultra (Ultrafast Pyrolysis)	1000	Very high	< 0.5	Chemicals, gas
Flash-gas	< 650	High	< 1 sec	chemicals, gas
Flash-liquid	< 650	High	< 1 sec	Bio-oil
Methane Pyrolysis	> 700	High	< 10 sec	Chemicals
Hydro Pyrolysis	< 500	High	< 10 sec	Bio-oil
Vacuum	400	Medium	2-30 sec	Bio-oil

ote: Generally, at low temperatures (< 450°c) at low heating rate, high yields of biochar is obtained. However, at high heating and high temperatures, gases are formed are the primary products. Bio-oils are formed at high heating rates and at intermediate temperatures.

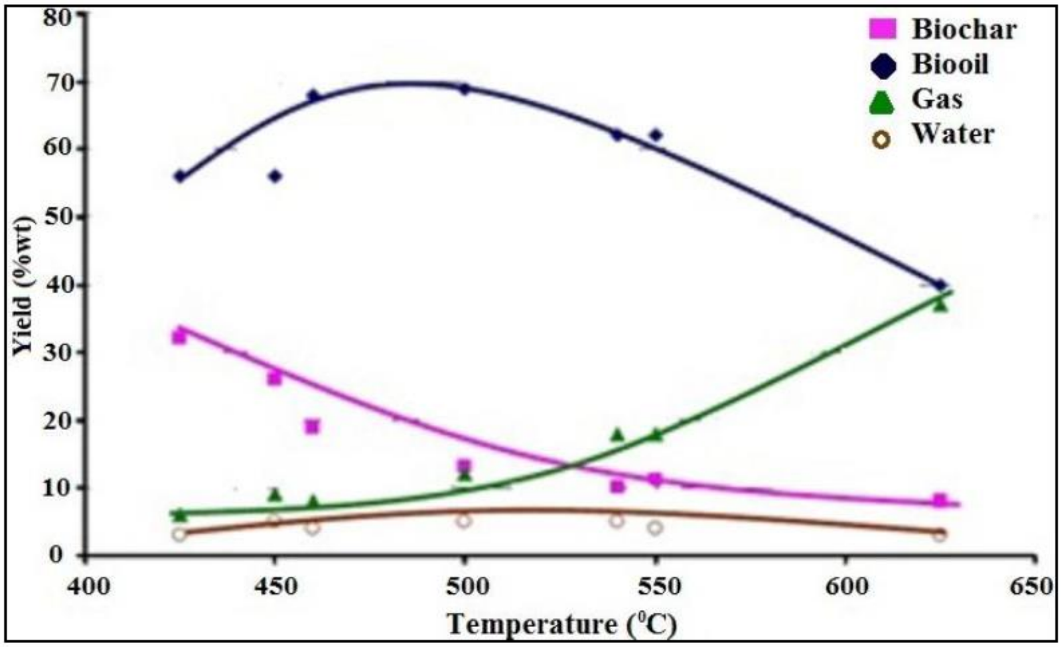


Figure-A: The % yield of the end products in the pyrolysis of biomass.

* **Mechanism of Pyrolysis** (Figures-2)

- biomass pyrolysis takes place through a ~~series~~ number of chemical reactions including reactions in parallel as well as in series
- the reactions are dehydration, aromatisation, isomerisation, depolymerization, decarboxylation and char formation
- in general, it is believed that the reaction consists of three stages;
  - the evaporation of free moisture (drying)
  - primary reaction — depolymerization, fragmentation, and formation of char
  - secondary decomposition — depolymerization, vapor cracking

✓ ① evaporation of free moisture (see figure - ~~1a~~ 2)

- biomass loses free moisture initially before any physical or chemical conversion
- dehydration starts at 100°c leaving behind amorphous carbon

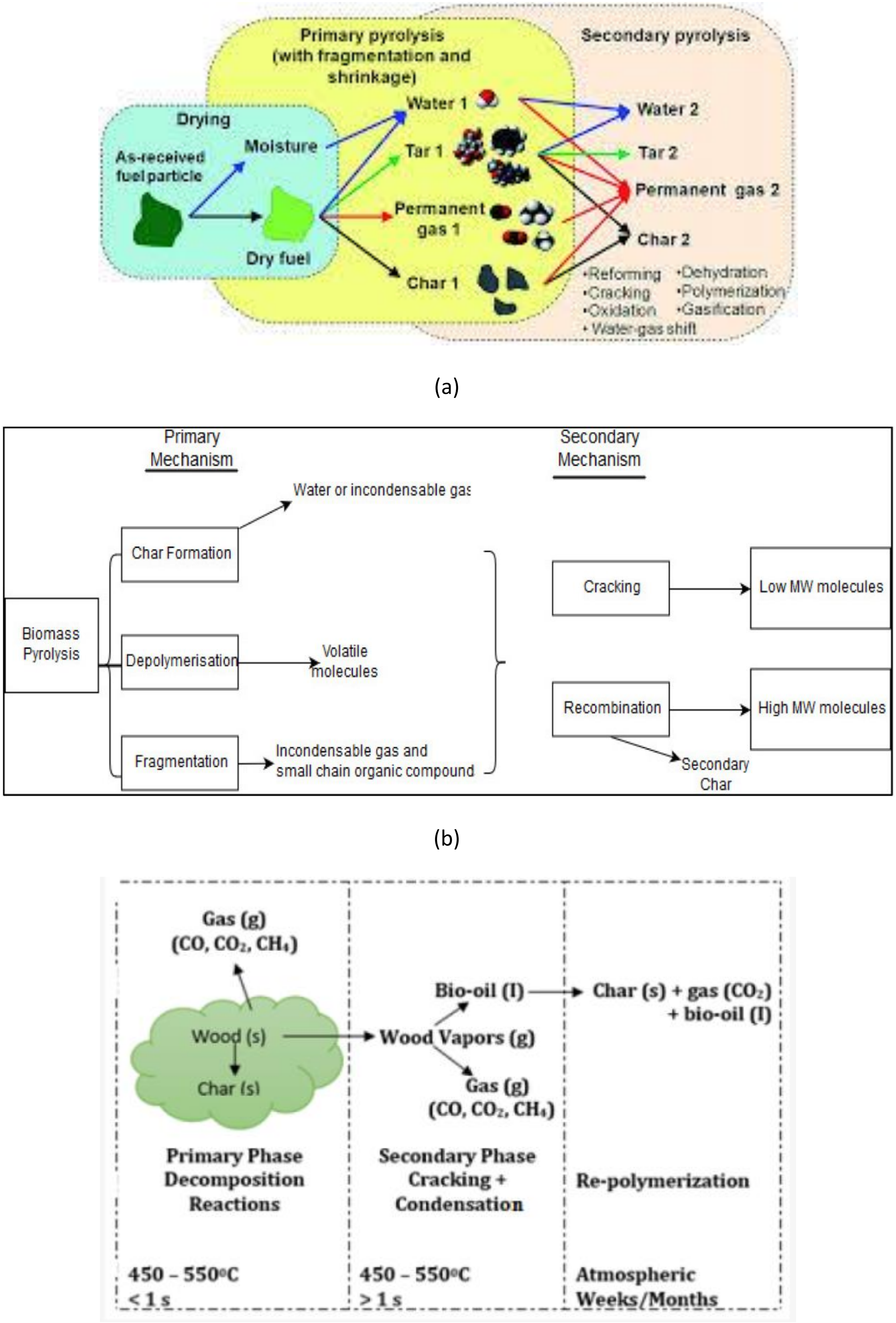
✓ ② primary reactions of biomass pyrolysis

- primary reaction starts after removal of moisture
- chemical bonds are broken ~~in the~~ resulting in the release of some volatiles and rearrangement of reactions
- primary reactions occur which include char formation, depolymerization and fragmentation
- biochar is left after release of condensible and non-condensible gases
- release of volatiles is recovered in the form of liquid fraction
- reactions occur between 250 - 500°c

✓ ③ — secondary degradation

- products generated during all primary reactions are not stable and thus undergo secondary degradation
- reactions under secondary degradation are: generally recombination (repolymerization) or cracking

Mechanism of Pyrolysis



(a)

(b)

(c)

Figures-2: Mechanism of pyrolysis.

* Sources of Biomass Feedstock for Pyrolysis

- biomass energy is recognized as the third largest source of energy
- many of the developing countries have been largely occupied by forest and agriculture land where 40-50% of energy is based on biomass
- the sources of biomass include many natural and derived materials such as:
  - agricultural crops and residues
  - forest wood and leaf residues
  - municipal solid wastes
  - forest and mill residues
  - animal residues and sewage
  - acquatic plants, and so on.....
- the physical and chemical properties of biomass is highly significant for product distribution
- Table-II & Table-III ~~so~~ show the properties of some biomass
- figure 3 reflects the available sources of biomass
- highest biochar yield is achieved when the biomass feedstock with high lignin content is pyrolysed under moderate temperature ≈ 500°c
- biomass containing high volatile matter generates large amount of syngas (CO, H_2) and bio-oil
- fixed carbon content raises the formation of biochar
- moisture content in biomass effects the heating value and ~~and~~ and also influences product distribution.
- biomass consists of carbon, hydrogen, oxygen and nitrogen.
- in some cases sulfure may also be present
- in some biomass significant amount of inorganic species may also be present.
- the chemicals obtained from co-products and residues may improve the biomass production chains
- various economic sectors such as agribusiness, petrochemi

Table-II: Physical Characteristics of Biomass

Feedstock	Density (kg/m^3)	Moisture Content (%)	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)
Wood	380	20	0.4–1	82	17
Bituminous coal	700	11	8–11	35	45
Wheat straw	18	16	4	59	21
Barley straw	210	30	6	46	18
Pine	124	17	0.03	-	16
Polar	120	16.8	0.007	-	-
Switchgrass	108	13–15	4.5–5.8	-	-

Table-III: Chemical Characteristics of Biomass

Feedstock	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Ash (%)
Wood	51.6	6.3	41.5	0.1	1
Bituminous coal	73.1	5.5	8.7	1.4	9
Wheat straw	48.5	5.5	3.9	0.3	4
Barley straw	45.7	6.1	38.3	0.4	6
Pine	45.7	7	47	0.1	0.03
Polar	48.1	5.30	46.10	0.14	0.007
Switchgrass	44.77	5.79	49.13	0.31	4.30

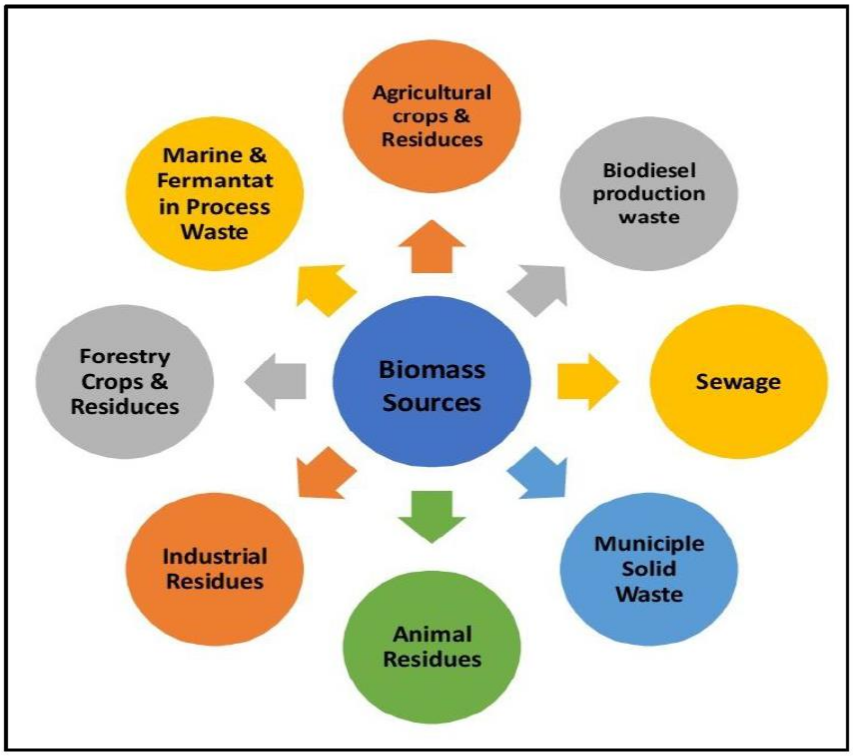


Figure-3: Available sources of biomass.

* Classification of Pyrolysis

- based on the residence time, rate of heating, particle size and temperature, there are basically three types of pyrolysis:
    - slow or conventional
    - Fast pyrolysis/Flash Pyrolysis
    - Intermediate Pyrolysis
- Tabe-4, below demonstrates some operating parameters for three types of pyrolysis process:

TABLE-~~3~~4

Process	Time (s)	Rate (K/s)	Size (mm)	Temperature (K)	Oil Yield	char yield	Gas Yield
Slow	450-550	0.1 — 1	5 - 50	550-950	30	35	35
Fast	0.5—10	10 - 200	< 1	850-1250	50	20	50
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

- slow pyrolysis or conventional pyrolysis
    - the main products are bio-oil, biochar and biogas
    - dominated by biochar yield (i.e. the main product)
    - temperature is kept as low as 400°C or above 400°C
    - operated under high residence time between 5-30 min
    - leads to secondary reaction of products in vapor phase with subsequent formation some bio-oil and bio-char
- fast pyrolysis
    - occurs with the use of short residence time ~ 0.5-10 s seconds
    - operates at temperatures between 577 - 977°C
    - very high heating rates are the main features
    - depending on the feedstock of biomass, gaseous, liquid and solid products range between 10-20, 60-75 and 15-75% respectively
- intermediate pyrolysis process
    - moderate temperature arround 500°C is suitable for the process.
    - the operating condition offers a wide range of variation
    - mostly conducted in fixed bed batch reactors for residence time varying from ~ 10-20 seconds.

- note: types of pyrolysis such as rapid, ultrafast and flash pyrolyses have also been discussed in the literature.

* Pyrolysis Products and their Applications

- pyrolysis of biomass results in three primary products:
  - char or bio-char (solid product)
  - bio-oil (the condensed liquid product)
  - permanent gases or biogas (syngas)
- biomass pyrolysis products yield may be improved
  - biochar yield improvement by applying less temp. keeping lower heating rate
  - bio-oil yield is enhanced by lower temperature but higher heating rate
  - gaseous products are improved by higher temperature at lower heating rate

→ Biochar

- production of biochar is an emerging bioresource technology for improvement of "food security" and mitigation of "climatic change"
- potential benifits of biochar as soil enrichment may be highlighted as:- addressing issues such as:
  - i. waste management
  - ii. biorefinery production
  - iii. increased soil fertility through through alteration of soil pH
  - iv. retention of nutrients through cation adsorption
  - v. reduction of emission of nitrous oxide (N_2O).
- as a promising modifier to soil, biochar has attracted the attention of policymakers in USA, Japan, Europe and in some developing countries.
- concised benifits of biochar for agriculture sector is summarized in Table-5:

→ Bio-oil

- it is the main product of biomass pyrolysis process
- there is a very current demand to convert biomass into bio-oil in order to use in ships, trains and aeroplanes
- reactor designs are the primary target of researchers to obtain a better quality bio-oil

Table-5: Application of Biochar in Agricuture Sector

- Reduced nitrogen leaching in groundwater
- Possible reduced emissions of nitrous oxide
- Increased cation exchange capacity resulting in better soil fertility
- Moderation of soil acidity
- Greater water retention
- Increase in the number of beneficial soil microbes

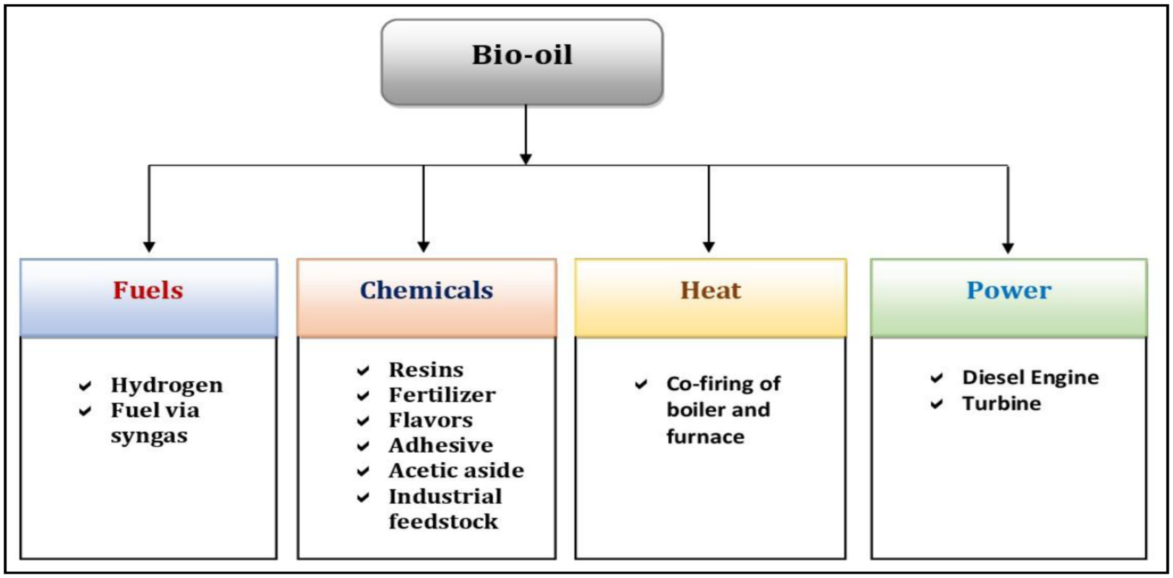
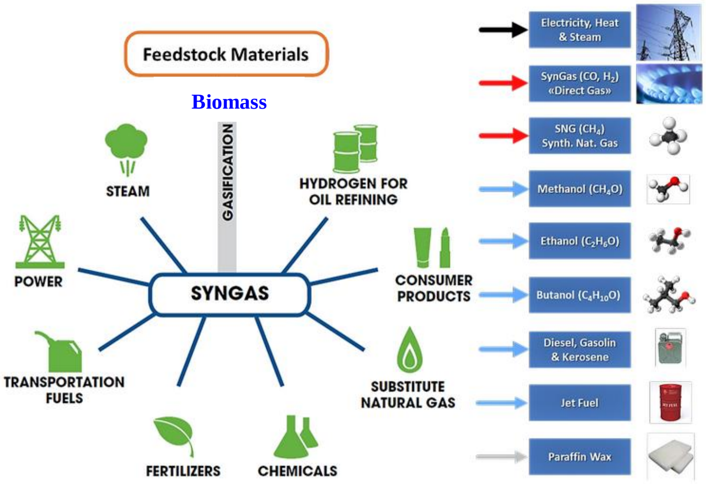


Figure-4: Various applications of pyrolysis bio-oil.

− **Biogas (Syngas)**

i. around 10–35% of biogas is produced in slow pyrolysis process
ii. it can be sued as an alternative renewable source of fuel in industrial combustion processes, as well as for internal combustion (IC) engines
iii. can be used as fuel in converted commercial petrol and diesel engines
iv. biogas yield is highly influenced by the pyrolysis temperature, and it is possible to achieve ahigher yield in flash pyrolysis with high temperatures
v. higher temperatures favour tar decomposition and the thermal cracking of tar to increase the proportion of biogas
vi. biogas mainly consists of hydrogen (H_2) and carbon monoxide (CO), it is also known as syngas.
vii. it may also contain a small volume of nitrogen (N_2), water, carbon dioxide (CO_2), hydrocarbons such as C_2H_4, CH_4, C_2H_6, ash,tar, and so on
viii. which depend on biomass feedstock and pyrolysis conditions

Broad applications demonstrated in the Figure-5, below:



* Pyrolyzers used in the Pyrolysis Process

- pyrolyzers (reactors) are the heart of biomass pyrolysis process
- it is the core of the pyrolysis technology where lot of attention has been paid by research community for advancement
- currently, many types of reactors have been designed mostly with the aim to maximize the product yield of bio-oil
- lately, many types of pyrolyzers have been developed, the main being the fluidized bed reactors (bubbling & circulating)
- the general classification of pyrolyzers are batch or continuous
- the classification may be summarized as:
  - fixed bed reactor
  - fluidized bed reactor
  - ablative reactor
  - vacuum pyrolysis reactor
  - rotating cone reactor
  - auger pyrolysis reactor

- fixed bed reactor
  - it is a simple, reliable, and proven system customarily used for production of biochar (shown in Figure-6)
  - consists of a gas cooling and cleaning system
  - generally operates with high carbon preservation, low gas velocity, and low resi conveyed over a long solid residence time
  - the basic units are drying, granulation, heating and cooling
  - the system operates between the temperatures are 450 to 750°c.
  - heating rate fluctuates between 5 and 100°c/min
  - the temperature ensures that the variables such as temperature program, heating rates, and residence

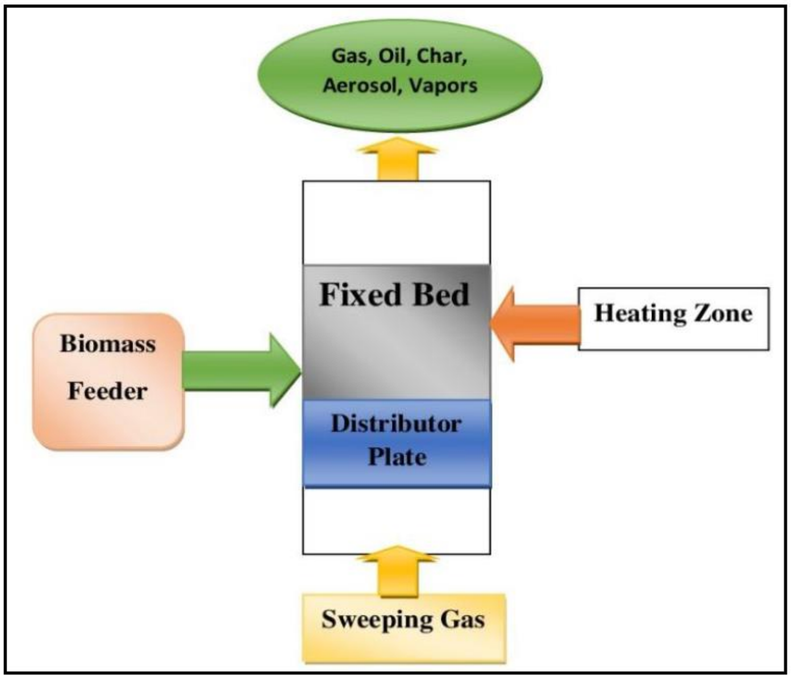
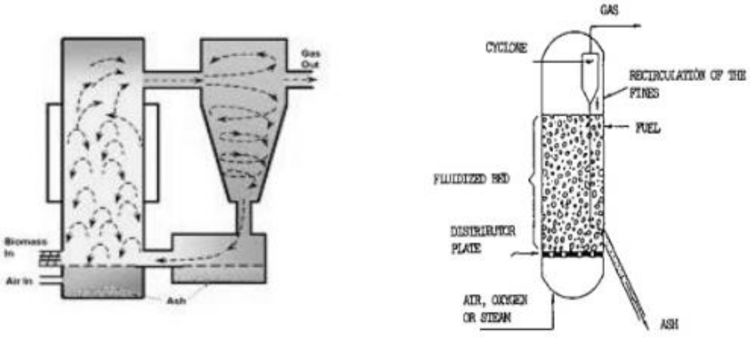


Figure 6. Fixed bed reactor.

−Fluidized Bed Reactor

- fluidized bed reactors (bubbling and circulating) have a well-known technology
- they have a series of industrial applications
- they are used in many projects in order to maximize the liquid product (bio-oil)
- as biomass has a very low density, it is common in fluidized bed reactors to use an inert element,
  usually sand, to give fluid dynamic stability to the process and help biomass heating
- the fluidised bed reactor comprises a fluid–solid blend that shows similar properties to the fluid
- fluidised bed reactors seem to be widespread and popular because they offer rapid reaction and heat transfer, a wide and high shallow area of contact between the fluid and solid,
- different types of fluidized bed reactors are available which include bubbling fluidized bed reactors and circulating fluidized bed reactors (figures-7)

➢ Fluidised Bed Gasifier
- Bubbling fluidised bed
- Circulating fluidised bed



Circulating fluidised bed

Bubbling fluidised bed

−Ablative Reactor (Figure-8)

- ablative pyrolysis is primarily dissimilar from fluid bed procedures in the absence of a fluidizing gas
- material connected to the wall fundamentally melts, and the residual oil evaporates as pyrolysis vapours.
- ahe ablative pyrolysis reactors have good heat transfer with high heating rates and a relatively small contact surface.
- they also have high energy and cost efficiency
- as no heating and cooling of fluidizing gases is required, furthermore, they tolerate fixing of condensation units with a small volume in requiring less space at lower costs.
- high pressures are needed for this type of process, and temperatures are usually under 600 °C; there is no ceiling to the particle size parameter for this type of reaction, but this type of pyrolysis reaction requires very high heat at the reactor wall.
- this type of pyrolysis does not require <u>inert gas</u> throughput for collection of the product gases

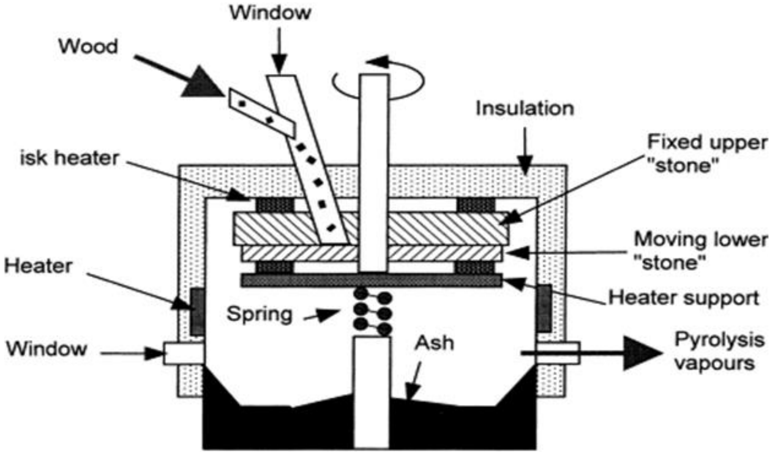
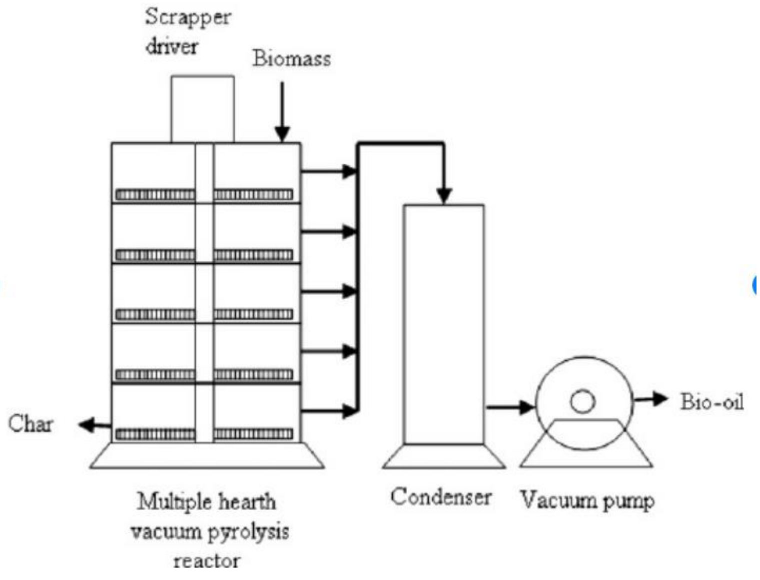


Figure-8: Ablative reactor.

−Vacuum Pyrolysis Reactor (Figure-9)

- represents a sluggish pyrolysis process with lower heat transfer rates conveyed with the fluidised bed technologies
- an induction and burner heater is used with molten salts
- the vapours formed are quickly detached from the vacuum
- itis categorized by lengthier residence time
- it is known to produce larger particles than most fast pyrolysis reactors
- there is also no requirement for carrier gas, and the process is mechanically complicated
- it needs high investment costs
- consistent operation of vacuum pyrolyser entails a superior feedstock input apparatus which discourages latent investors



Process schematic for vacuum pyrolysis.

Figure-9: Vacuum Pyrolysis Reactor

−Rotating Cone Reactor

- it is a rotating cone reactor innovative reactor for flash pyrolysis with tiny char formation
- biomass feedstocks, such as rice husks, wood, palm kernel, coffee husk, and so on, can be milled in the rotating cone reactor
- there is no big scale of commercial implementation for a rotating cone reactor
- high-speed rotation provokes dynamic mixing of biomass that sequentially proceeds to fast heat transfer
- Figure-10 shows the rotating cone reactor

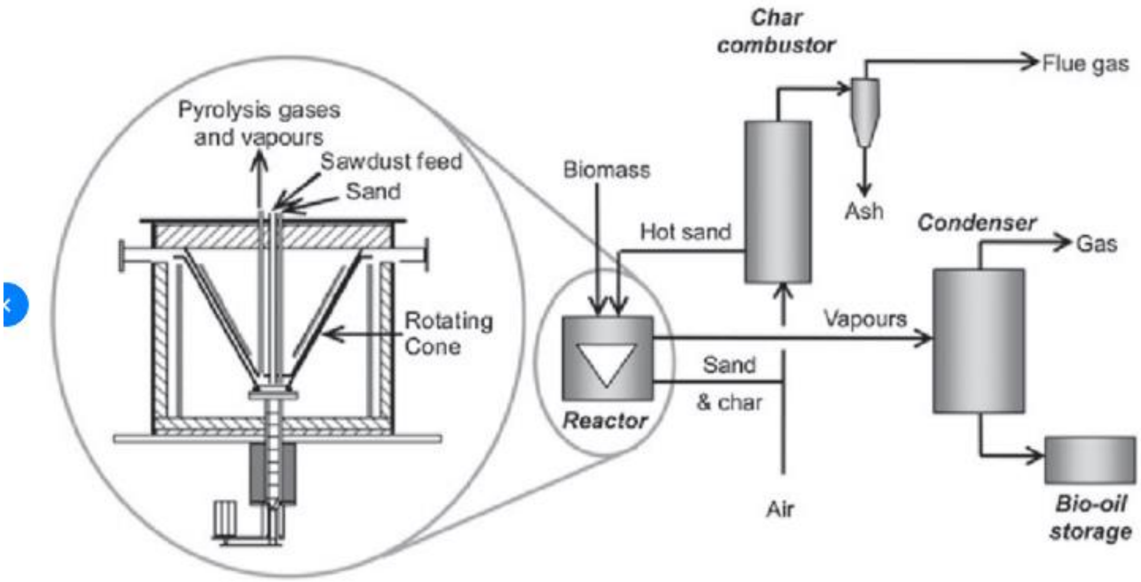
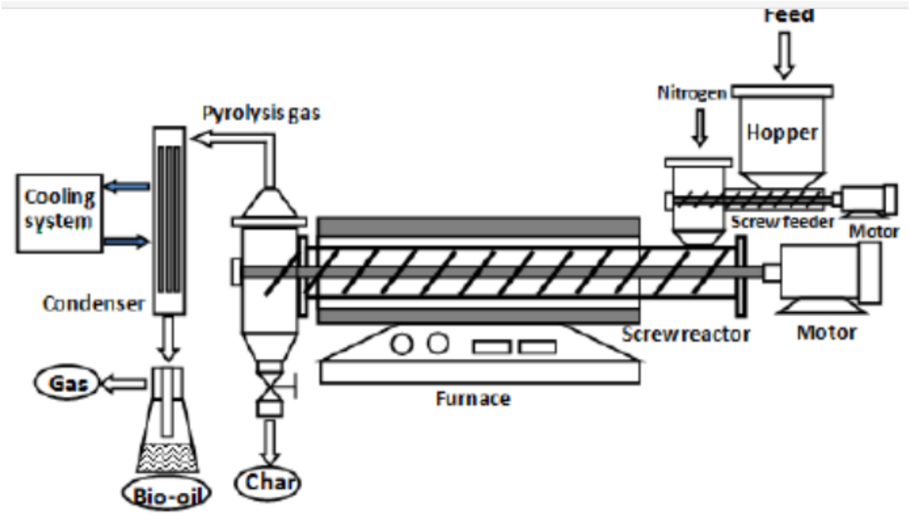


Figure-10: Rotating cone pyrolyser.

−Auger Reactor

- it is used to used to interchange biomass feedstock over an oxygen-free cylindrical tube
- in this pyrolyzer system, vapour residence time could be altered by fluctuating the heated zone
- auger reactors are getting attention of many mid-size industries
- stirring parts in the hot precinct and temperature transmission on a large scale are the major challenges for the auger reactors
- Figure-11 shows the auger reactor



− Comparison of various Pyrolyzers

The comparison is shown in the Table-6, below:

Table-6: Comparison of Various Biomass Pyrolysis Reactors Based on overall Performance and Efficiency

Pyrolyser	Status (units)	Bio-Oil Yield (wt %)	Operational Complexity	Particle Size	Biomass Variability	Scale-Up	The Inert Gas Flow Rate
Fixed bed	Pilot (single), lab (multiple)	75	Medium	Large	High	Hard	Low
Fluidised bed	Demo (multiple), lab (multiple)	75	Medium	Small	Low	Easy	High
Recirculating bed	Pilot (multiple), lab (multiple)	75	High	Medium	Low	Hard	High
Rotating cone	Demo (single)	70	Medium	Medium	High	Medium	Low
Ablative	Pilot (single), lab (multiple)	75	High	Large	High	Hard	Low
Screw/auger reactor	Pilot (multiple), lab (multiple)	70	Low	Medium	High	Easy	Low
Vacuum	Pilot (single), lab (few)	60	High	Large	Medium	Hard	Low

∗Current Status of Pyrolysis Technology

- depleting condition of fossil fuels, food security and environmental concerns have posed great challenge to world community
- not only the quality, but the sustenance of life is under threat
- biomass pyrolysis will possibly help reduce CO_2 and the world's dependence on oil production
- bio-oils have the potential to lower CO_2 discharges; they are derived from plants which use CO_2 for growing
- an amalgamation of technologies is required to assimilate reactor design and operational procedure to recover the efficiency of biomass
- fast pyrolysis systems process small elements to maximize bio-oil yield, whereas low pyrolysis technologies use wood to produce char chunks
- the recognition of the environmental matters are allied with the use of carbonization technologies and the technical difficulties of operating fast pyrolysis reactors
- intermediate pyrolysis reactors propose prospects for the extensive balanced production of bio-oil and char
- presently, the foremost interests in pyrolysis technology are for CO_2 mitigation, electricity generation from biomass, and energy independence
- the pyrolysis technologies can be considered as slow, intermediate, fast, and flash pyrolysis but, then again, the most frequently used systems, meanwhile, are the fast and slow pyrolysis processes
- biochar is the key product of the slow pyrolysis, and transpires with moderate temperature, longer residence time, and small heating system rate
- dissimilarly, bio-oil is the key product of fast pyrolysis which formed with a fast heating rate within short residence time
- fast pyrolysis produces a higher quality and quantity of bio-oil than the slow pyrolysis
- it is expected that environmental and economic performance will increase the effectiveness of the pyrolysis process
- various actions are needed to overcome the technical challenges, including plummeting parasitic energy losses, improving pyrolysis reactor outlines, improving feedstock logistics, and enhancing biomass heating rate
- biomass feedstocks are most important to increase the pyrolysis products on a large scale
- this can be attained by producing energy-condensed products from biomass
- accumulation of metal and ash in reactor bed materials impedes pyrolysis which can reduce bio-oil yields
- controlling pyrolysis temperature and heating rate, and using smaller particle sizes can reduce accumulation
- recently, a study revealed that an ablative reactor can convert entire wood chips and produce more energy
- to conclude, cohesive pyrolysis systems that associate gasification or fast pyrolysis are one more important approach for making pyrolysis commercially viable and improving environmental performance
- Table-7 shows the available pyrolysis plants worldwide.

Table-7: Current Pyrolysis Plants Worldwide

Reactor Technology	Organisation/Location	Capacity (kg/h)	Desired Product
Fixed bed	Bio-alternative, USA	2000	Char
Bubbling fluidised bed	THEE	500	Gas
	Dyna Motive, Canada	400	Oil
	BEST Energy, Australia	300	Oil
	Wellman, UK	250	Oil
	Union Fenosa, Spain	200	Oil
	Zhejiang University, China	20	Oil
	RTI, Canada	20	Oil
	Waterloo University	3	Oil
	Zhejiang University, China	3	Oil
Circulating fluidised bed	Red Arrow, WI; Ensyn	1700	Chemicals
	Red Arrow, WI; Ensyn	1500	Chemicals
	Ensyn Engineering	30	Oil
	VTT, Finland, Ensyn	20	Oil
Rotating cone	BTG, Netherlands	200	Oil
	University Twente	10	Oil
Vacuum	Pyrovac, Canada	350	Oil
	Laval University	30	Oil
Ablative	PYTEC, Germany	250	Oil
	BBC, Canada	10–15	Char
	PYTEC, Germany	15	Oil
Vortex	Solar energy research Ins.	30	Oil
Another type	Fortum, Finland	350	Oil
	University Zaragoza	100	Gas
	Georgia Tech. Research Ins.	50	Oil

∗Future Challenges

- in order to achieve full potential of biomass pyrolysis technology, improved understanding and successful commercialisation, additional research and development are needed.
- a couple of issues such as the lack of markets for pyrolysis oils and lack of biochar-derived products with well-defined performance characteristics must be overcome
- it is recommended to speed up the improvement and deployment of bio-oil refineries
- the improvement of flexible designs for pyrolysis units for producing higher yields of the product is a technical challenge
- as different pyrolysis technologies have different ranges of product yields, the selection of pyrolysis technologies, feedstocks, and their operating parameters should be based on the economic trade-offs
- however, in addition to the fundamental challenges, a few more important challenges for future biomass pyrolysis research are listed below:
    - understanding the proper working of pyrolysis reactors and processes
    - development of a new reactor that is cost-effective and highly efficient
    - development of catalysts for bio-oil upgrading
    - development of proper solar system reactors
    - post-pyrolysis processing to improve product bio-oil properties
    - understanding the limitations and potential for improvements of the quality of products obtained by biomass pyrolysis

- development of both fast pyrolysis and bio-oil upgrading, ensuring these are focused on delivering useful and valuable products

For the full implementation of pyrolysis technology, more research is needed to determine designs that will remove oxygen in the gas phase from pyrolysis oil. Pyrolysis technology has the potential to be applied in a vast diversity of situations and, through this process, diversity of products can be obtained. Hence, it is quite difficult to explore a sustainable design for all prospective applications. In addition, balanced financial investments to create new knowledge, technology, and markets for the purpose of building a united vision for the utilisation of pyrolysis technologies is crucial.

energies

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Review

An Overview of Recent Developments in Biomass Pyrolysis Technologies

M. N. Uddin [1], Kuaanan Techato [2,3], Juntakan Taweekun [4], Md Mofijur Rahman [5,6,*], M. G. Rasul [5], T. M. I. Mahlia [6] and S. M. Ashrafur [7]

[1] Sustainable Energy Management, IGES, Prince of Songkla University, Hatyai, Songkhla 90110, Thailand; 5910930005@psu.ac.th
[2] Environmental Assessment & Technology for Hazardous Waste Management Research Center, Faculty of Environmental Management, Prince of Songkla University, Hatyai, Songkhla 90110, Thailand; kuaanan.t@psu.ac.th
[3] Center of Excellence on Hazardous Substance Management (HSM), Bangkok 10330, Thailand
[4] Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hatyai, Songkhla 90112, Thailand; jantakan.t@psu.ac.th
[5] School of Engineering & Technology, Central Queensland University, Rockhampton, QLD 4701, Australia; m.rasul@cqu.edu.au
[6] Faculty of Engineering and Information Technology, University of Technology, Sydney, NSW 2007, Australia; TMIndra.Mahlia@uts.edu.au
[7] Biofuel Engine Research Facility (BERF), Queensland University of Technology, Brisbane, QLD 4000, Australia; s2.rahman@qut.edu.au
* Correspondence: m.rahman@cqu.edu.au; MdMofijur.Rahman@uts.edu.au

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Abstract: Biomass is a promising sustainable and renewable energy source, due to its high diversity of sources, and as it is profusely obtainable everywhere in the world. It is the third most important fuel source used to generate electricity and for thermal applications, as 50% of the global population depends on biomass. The increase in availability and technological developments of recent years allow the use of biomass as a renewable energy source with low levels of emissions and environmental impacts. Biomass energy can be in the forms of biogas, bio-liquid, and bio-solid fuels. It can be used to replace fossil fuels in the power and transportation sectors. This paper critically reviews the facts and prospects of biomass, the pyrolysis process to obtain bio-oil, the impact of different pyrolysis technology (for example, temperature and speed of pyrolysis process), and the impact of various reactors. The paper also discusses different pyrolysis products, their yields, and factors affecting biomass products, including the present status of the pyrolysis process and future challenges. This study concluded that the characteristics of pyrolysis products depend on the biomass used, and what the pyrolysis product, such as bio-oil, can contribute to the local economy. Finally, more research, along with government subsidies and technology transfer, is needed to tackle the future challenges of the development of pyrolysis technology.

Keywords: renewable energy; biofuel; environment; technology development

1. Introduction

Nowadays, energy usage is prodigious, and a significant key factor for the advancement of a nation, and the scarcity of energy has become an economic threat for the development of nations around the world [1,2]. It is said that "Energy is a critical component of our lives. Without energy, we can't even dream of economic growth. But despite its central role, not everyone has access to modern energy services" [3,4]. Today's energy requirement is increasing in trend, due to population growth and ongoing economic and technological advancement around the world [4]. Currently, fossil fuels are the main source of energy because of their high calorific values, good anti-knocking properties, and high heating values; meanwhile, reserves are limited. Therefore, the development of alternative energy resources can lower the depletion of fossil fuel by reducing their consumption [5–7]. On the other hand, the world's heating condition is increasing every day. The atmospheric CO_2 level has crossed the risky level that was forecast to happen in another 10 years [8]. Furthermore, the depletion of fossil fuels and extreme change of climate have driven the search for alternative energies and renewable energy sources that can meet the world's energy demand, reduce greenhouse gas emissions, curb pollution, and maintain the planet's temperature at a stable level [9–11].

Among the alternative energy sources, biomass can become a promising sustainable energy source, due to its high diversity and availability [12]. Biomass can be defined as all biodegradable organic material derived from animals, plants, or microorganisms. This definition also includes products, by-products, waste originating in agricultural activities, as well as non-fossil organic waste produced by industrial and municipal waste [13]. Biomass is the third most important source used to generate electricity and thermal applications [14,15]. The most common biomass feedstocks are banana peel, rice and coffee husks, sugarcane bagasse, palm oil processing residues, and the waste of animals [16,17]. Biomass can be considered as a blend of organic resources and minor amounts of minerals, which also contains carbon, oxygen, hydrogen, nitrogen, sulphur, and chlorine [18].

Different types of energy can be produced through the thermal conversion of biomass, such as combustion, pyrolysis, gasification, fermentation, and anaerobic decomposition. Combustion is a thermochemical process used for the production of heat, which consists of a chemical reaction in which a fuel is oxidised, and a large amount of energy is released in the form of heat (exothermic reaction). Pyrolysis is a thermal decomposition process which takes place in the absence of oxygen [19,20]. In combustion and gasification processes, the first step is pyrolysis, followed by total or partial oxidation of primary products. Gasification is the process of generating electricity by applying heat to organic material in the presence of less oxygen. In the fermentation process, organic materials are used to produce alcohol, with the help of yeast, to generate power in automobiles. Anaerobic decomposition is the process of producing biogas, and generates electricity.

Among all the conversion techniques of biomass conversion, the pyrolysis process offers a number of benefits, including less emissions and that all the by-products can be reused. In addition, during the process, pyrolysis produces solid or carbonised products, liquid products (bio-oils, tars, and water) and a gas mixture composed mainly of CO_2, CO, H_2, and CH_4 [21–23]. The oil resulting from the pyrolysis of biomass, usually referred to as bio-oil, is a renewable liquid fuel, which is the main advantage over petroleum products. It can be used for the production of various chemical substances [24]. The pyrolysis process has three stages: the dosing and feeding of the raw material, the transformation of the organic mass and, finally, the obtaining and separation of the products (coke, bio-oil, and gas). The factors that influence the distribution of the products are the heating rate, final temperature, composition of the raw material, and pressure [25].

The pyrolysis process has great market potential; in this process, biomass is used as raw material in order to produce energy. Therefore, intense research is taking place around the world to improve this method of energy production. Among the technologies, such as digestion, fermentation, and mechanical conversion, thermo-conversion for producing energy from biomass is relatively newer from a commercial perspective, and gaining more attention because of its technical and strategical advantages. In addition, the production of waste is constantly increasing, and the economic activity linked to it is becoming increasingly important. The elimination or attenuation of environmental problems and obtaining profitability in the process of managing them is a very favourable step. Therefore, pyrolysis could be an alternative means of energy recovery, obtaining different fractions that are also recoverable not only from the energy point of view.

Though the research into pyrolysis technology indicated that pyrolysis is a more promising option to the sustainable development, pyrolysis technology still needs further improvement, and several challenges need to be tackled to gain its full potential benefits. Furthermore, several types of research have been carried out recently, focusing on the use of pyrolysis technology, but only a few papers have been analysed and reviewed by the researchers. Thus, the main aims of this study are to present a brief review of the development of pyrolysis technology, including their present status and future challenges, to provide information to the researchers who are interested in pyrolysis technology. A number of studies from highly rated journals in scientific indexes are reviewed, including the most recent publications.

2. Biomass Pyrolysis

Biomass is a renewable source for the production of energy, and it is profusely obtainable everywhere in the world [26,27]. The sustainable use of biomass energy is an alternative to partially replace the use of fossil fuels and nuclear energy. Rural people in developing countries, representing about 50% of the global population, depend on biomass energy [9]. Biomass assists the world in meeting greenhouse gas reduction goals [9,28,29]. The increase in availability and technological developments of recent years allow the use of biomass as a renewable energy source with low levels of emissions and environmental impacts. Biomass energy can be in the forms of biogas, bio-liquid, and bio-solid fuels. It can be used to replace fossil fuels in power and transportation. It is considered as a renewable energy source because the energy mainly comes from the sun and, also, it needs a short time period to re-grow.

Pyrolysis process is mainly characterised by solid fuel thermal degradation, which involves the rupture of carbon–carbon bonds and the formation of carbon–oxygen bonds. Pyrolysis requires temperatures of up to 400–550 °C, although it can be done at temperatures even higher [30–33]. Figure 1 shows the percentage yield during the pyrolysis of biomass.

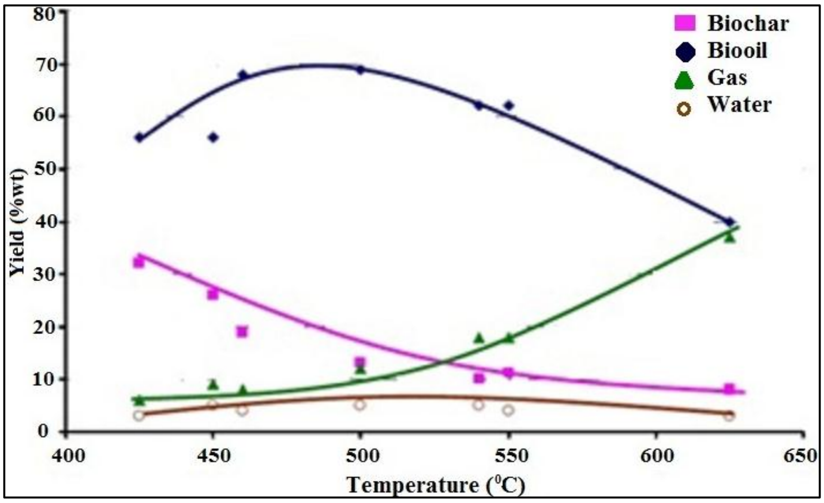

Figure 1. The % yield of the end products the pyrolysis of biomass [9].

One part of the biomass is reduced to carbon, while the remaining part is oxidised and hydrolysed to carbohydrates, phenols, aldehydes, ketones, alcohols, and carboxylic acids, which combine to form more complex molecules such as esters, polymer products, and others [34–36]. Pyrolysis can be achieved by the complete absence of the oxidising agent. The practice of using air to perform pyrolysis is achieved by feeding air in an amount below stoichiometric; combustion occurs in only a small part of the biomass and, thus, the heat released in the combustion is used to keep the temperature of the reactor constant, while processing the reactions related to pyrolysis [37].

The products formed during pyrolysis, namely, coal fines, gases, acid extract, and bio-oil, have high calorific value, and have had several applications in both the chemical and power generation industries. In ancient Egyptian times, the pyrolysis process was used to generate tar for sealing boats [16], and the ancient Egyptians performed wood decontamination by assembling tars and pyrolignous acid for use in their mummifying industry [38,39]. Pyrolysis has gained more attention as an effective and practical method in converting biomass into bio-fuel recent years [40]. Pyrolysis is not only part of the combustion and gasification processes, but it is also the first stage of both of these processes. The gas is composed of carbon monoxide, carbon dioxide, and light hydrocarbons. This dark-coloured liquid is called bio-oil and charcoal solid. The yields and quality of the products are influenced by the operating conditions. Pyrolysis receives different denominations depending on the conditions used. In slow pyrolysis or carbonisation, low temperatures and long residence times are employed, favouring the production of charcoal. High temperatures and long residence times favour the formation of gases. Whereas moderate temperatures and low residence time of the gases favour the production of liquids (bio-oil). Figure 2 shows the chemical reaction during the pyrolysis process.

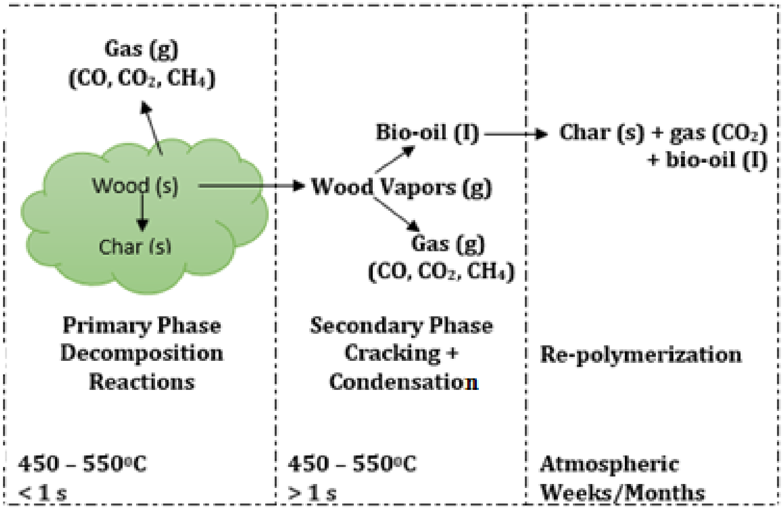

Figure 2. Representation of the reaction paths for wood pyrolysis [41].

3. Mechanism of Pyrolysis Process

The biomass pyrolysis can be divided into two categories, such as primary and secondary mechanisms [41]. Figure 3 shows the detailed mechanism of the pyrolysis process. In the primary mechanism, volatile compounds are released, while the chemical bonds within the polymers are broken during biomass heating process [42,43]. Furthermore, rearrangement reactions within the matrix of the residue take place. Some of the volatile compounds which are unstable further undergo additional reactions, which are defined as a secondary mechanism.

The primary mechanism can be described using three different approaches, namely char formation, depolymerisation, and fragmentation. In the char formation process, initially, benzene rings are formed, and these rings combine into a solid residue known as char, which is an aromatic polycyclic structure [44]. During this process, water or incondensable gas is also released [45,46]. In the depolymerisation process, the polymers are broken into monomer units, which reduce the degree of polymerisation. This process continues until the volatile molecules are produced [47]. Finally, in fragmentation, incondensable gas and small chain organic compounds are formed through the linkage of many covalent bonds of the polymer, even within the monomer units [42].

The secondary mechanism consists of cracking, recombination, and others [42,48]. In cracking, lower molecular weight molecules are formed by breaking volatile compounds [49]. By contrast, in the recombination process, volatile compounds combine into high molecular weight compounds, which may or may not be volatile [43,50]. In some cases, a secondary mechanism leads to the formation of secondary char [48,51].

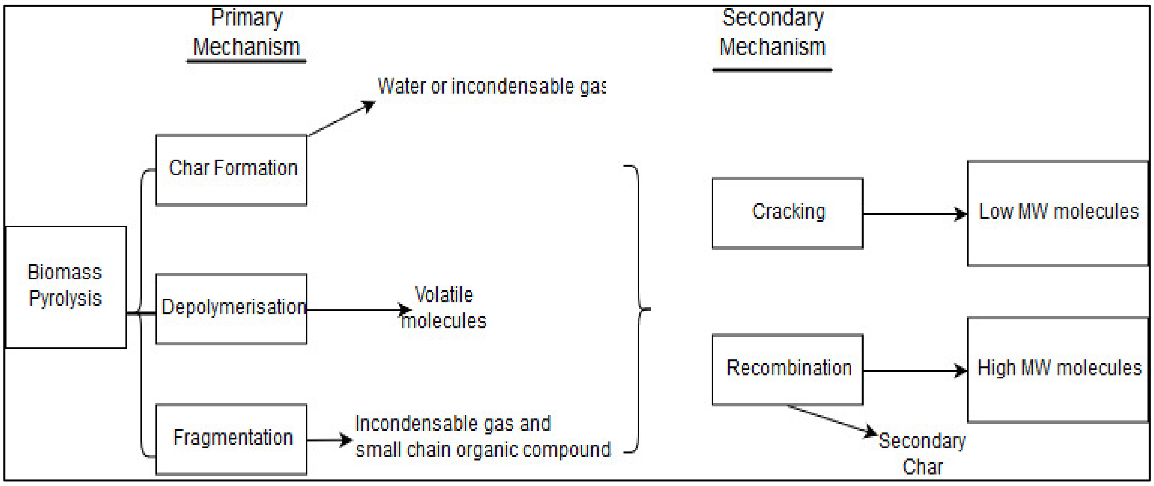

Figure 3. The detailed mechanism of the pyrolysis process.

4. Sources of Biomass and Their Properties

Biomass energy is currently recognised as the third largest global energy source. In many developing countries which have significantly large forest and agricultural land, 40–50% of energy usage is based on biomass. Green plants can directly/indirectly produce biomass using the photosynthesis process, by transforming sunlight into plant material [29,52]. The resources of biomass include various natural and derived materials, such as agricultural crops and residues, forest wood and leaf residues, municipal solid wastes (MSW), forest and mill residues, animal residues, and sewage. Agricultural crops and wastage (sugarcane, cassava, and corn) provide carbohydrate and starch. Roughly, the biomass species contain woody biomass, straw, beech wood, seedcakes, bagasse, and municipal solid waste (MSW) [53–59]. The available sources of biomass are shown in Figure 4.

Biomass is a very versatile feedstock in its morphology and physical characteristics. It can be quite wet or dry dense or fluffy, high or low ash containing, small in shape or large, homogeneous or inhomogeneous, and so on. This makes the use of biomass fuels in dedicated gasifier reactors quite difficult and, in most cases, some pre-treatment of the biomass is needed. The feedstocks used for pyrolysis and their physical and chemical properties are more important. The highest bio-char yields are achieved when feedstocks with high lignin content are pyrolysed at moderate temperatures (approx. 500 °C). Furthermore, some other indicators of pyrolysis product yields are the ratios of fixed carbon, moisture, volatile matter, and ash content. Generally, biomass containing significant volatile matter offers a large amount of syngas and bio-oil, while fixed carbon raises the production of biochar. Moisture content in biomass influences the heat transfer process, as well as significantly affects product distribution. Tables 1 and 2 show the physical and chemical properties of biomass. Biomass consists of elements such as carbon, hydrogen, oxygen, and nitrogen. Sulphur is present in smaller proportions, and some types of biomass also contain significant portions in inorganic species. The chemicals obtained from co-products and residues can improve the biomass production chains, due to the strategic participation of the chemical industry in the supply of inputs and final products to various economic sectors, for example, agribusiness, petrochemical, automotive, pharmaceutical, cosmetics, civil construction, and so on [60].

Table 1. Physical characteristics of biomass [9].

Feedstock	Density (kg/m^3)	Moisture Content (%)	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)
Wood	380	20	0.4–1	82	17
Bituminous coal	700	11	8–11	35	45
Wheat straw	18	16	4	59	21
Barley straw	210	30	6	46	18
Pine	124	17	0.03	-	16
Polar	120	16.8	0.007	-	-
Switchgrass	108	13–15	4.5–5.8	-	-

Table 2. Chemical characteristics of biomass [9].

Feedstock	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Ash (%)
Wood	51.6	6.3	41.5	0.1	1
Bituminous coal	73.1	5.5	8.7	1.4	9
Wheat straw	48.5	5.5	3.9	0.3	4
Barley straw	45.7	6.1	38.3	0.4	6
Pine	45.7	7	47	0.1	0.03
Polar	48.1	5.30	46.10	0.14	0.007
Switchgrass	44.77	5.79	49.13	0.31	4.30

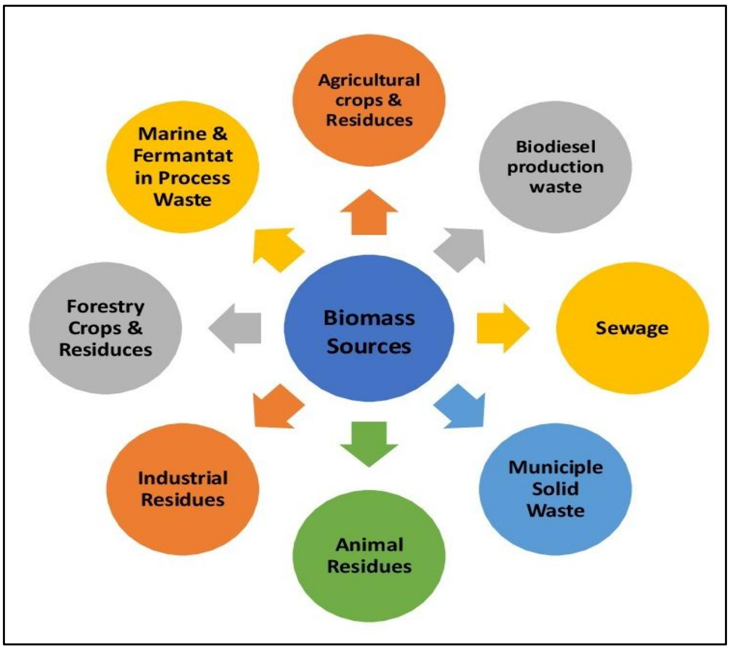

Figure 4. Available sources of biomass [61].

5. Pyrolysis Technology

Pyrolysis technology is the decomposition of heated organic matter in the absence of atmospheric oxygen, where heating is controlled by temperature ranges and provides the energy needed to break down the structures of the macromolecules present in biomass [62]. In the process of pyrolysis, biomass degradation occurs through heating, in which the formation of three products occurs: coal, oil, and pyrolytic gas, and, depending on the conditions in the reactor, one of these products can be maximised [63,64]. Currently, there are basically three pyrolysis processes in the world: slow pyrolysis, fast pyrolysis, and ultrafast pyrolysis. Biomass is first put into the reactor feed system, usually an endless screw. Then, the biomass enters the reactor and undergoes thermal degradation. Any gas that does not condense and has no energetic ends returns to the process and is used as entrainment gas in the reactor.

5.1. Slow Pyrolysis

Slow or conventional pyrolysis consists of systems known as "charcoal" or continuous systems, with slow biomass heating above 400 °C in the absence of oxygen [65]. In this process, the biomass is pyrolysed with low heating rates, around 5 to 7 °C/minimum, where the liquid and gaseous products are minimal, and the coal production is maximised [66,67]. Slow pyrolysis of wood, with a 24 h endurance, was a very common technology in industries until the early 1900s, where coal, acetic acid, methanol, and ethanol were obtained from wood [68,69]. Slow pyrolysis is characterised by small heating rates and a maximum temperature range of around 600 °C, and the biomass time in the reactor is between 5 and 30 min. The main products are bio-oil, coal, and gases [68].

5.2. Rapid Pyrolysis

Rapid pyrolysis is a promising method for conversion of biomass into a liquid product. The produced pyrolysis oil (bio-oil) is an intermediate dense energy fuel, which is possible to upgrade to hydrocarbons in diesel and gasoline [70]. In rapid pyrolysis, the biomass decomposes very quickly, generating mainly vapours and aerosols, and a small amount of coal and gas. After cooling and condensation, a homogeneous mobile dark brown liquid is formed, which has a calorific value corresponding to half of the conventional fuel oil [71]. Rapid pyrolysis technology is used globally, in large scale, for the production of liquids (bio-oils), and there is a lot of interest regarding this technology among biofuel researchers. Several reactors are used in the rapid pyrolysis process. Among them are the dragged-flow reactor, vacuum furnace reactor, vortex reactor, rotary reactor, bubbling fluidised bed reactor, and others; many researchers have contributed in the field of pyrolysis using one of these reactors [67].

5.3. Ultrafast Pyrolysis

The ultrafast pyrolysis has, as its main characteristics, very high heating rates and very low residence time of the biomass in the reactor. These characteristics favour the production of vapours, and make the process very similar to gasification. Due to the high heating rate, where biomass residence times are only a few seconds, reactors are needed to meet these heating needs [67]. These reactors have a fluidised bed and are flow-dragged. The fluidised bed reactor is used in the execution of multiphase chemical reactions, where a catalyst, usually sand, is used, working the same as with a fluid inside [72,73]. According to Laird et al. [65], ultrafast pyrolysis for coal production involves heating the biomass, under moderate to high pressure, in a reactor. In this particular case, the coal yield reaches 60%, and is volatile (bio-oil and synthesis gas) to 40%; this technology is more likely to use heat recovery equipment. Table 3, below, demonstrates some operating parameters of the three types of pyrolysis process [72,73].

Table 3. Operating parameters of different pyrolysis processes.

Process	Time (s)	Rate (K/s)	Size (mm)	Temp. (K)	Oil Yield	Char Yield	Gas Yield
Slow	450–550	0.1–1	5–50	550–950	30	35	35
Fast	0.5–10	10–200	<1	850–1250	50	20	30
Flash	<0.5	>1000	<0.2	1050–1300	75	12	13

5.4. Flash Pyrolysis

This process is also known as fast pyrolysis, due to the high speed of the process. However, in this process, not only kinetics play an important role, but heat and mass transfer processes, such as phase change phenomena, are also important. In this process, the biomass decomposes to generate mainly vapours, aerosols, and a certain amount of coke. After cooling and condensation, a dark brown liquid (bio-oil) is formed, with a calorific value that is half the value corresponding to that of diesel. Unlike traditional processes, this is an advanced process with carefully controlled parameters to obtain high liquid yields [74]. In order to carry out this process, the following must be observed: (a) subjecting the biomass particles to an optimum temperature so that they react, and (b) minimising their exposure to low intermediate temperatures that stimulate coke formation. One method to achieve these objectives is to use small particles, for example, those that are present in fluidised bed processes (a fluidised bed is a packed bed with a fine-grained solid). Another possibility is to transfer heat quickly, only to the surface of the particles that are in contact with the heat source, which is applied in ablation processes [75,76].

6. The Products of Pyrolysis Process

The pyrolysis of biomass produces three primary products, namely char, permanent gases, and vapours which condense to a viscous liquid (dark brown in colour) at ambient temperature. Biomass pyrolysis product yields can be improved as follows: (1) charcoal—less temperature and lower heating rate procedure, (2) liquid products—lower temperature but higher heating rate procedure, and (3) fuel gas—higher temperature and lower heating rate procedure. Table 4 shows the pyrolysis processes at different temperatures.

Table 4. Pyrolysis processes at different temperature.

Condition	Processes	Products
<350 °C	Free radical formation, water elimination, and depolymerisation	Formation of carbonyl and carboxyl, the evolution of CO and CO_2, and mainly a charred residue
350–450 °C	The split of glycosidic connections of polysaccharide by substitution	A combination of levoglucosan, anhydrides, and oligosaccharides as a tar segment
450–500 °C	Dehydration, rearrangement, and fission of sugar units	Formation of carbonyl compounds
>500 °C	A combination of all the above processes	A combination of all the above products
Condensation	Unsaturated products shrink and split to the char	A highly reactive char remainder comprising trapped free radicals

6.1. Bio-Oil

Bio-oil, also known as pyrolysis oil, crude bio-oil, pyrolytic tar, pyrolignous tar, pyrolignous liquor, wood liquid, wood oil, smoke condensate, and distilled from wood, is a dark brown-coloured liquid, almost black, with a characteristic odour of smoke, and an elemental composition similar to the biomass. It is a complex mixture, containing oxygenated compounds and a high volume of water, which originates from the moisture of the biomass and the reactions. It might also contain some amount of coal particles and dissolved alkali metals from the ash. The composition of the total mixture depends on the type of biomass, process conditions, equipment, and the efficiency in the separation of the coal and the condensation.

The bio-oil can be considered as a micro emulsion, in which the continuous phase is an aqueous solution of the products of cellulose and hemicellulose fragmentation which stabilises the discontinuous phase of the pyrolytic lignin macromolecules [71]. There is a very current and praising demand to convert biomass into liquid fuels in order to use in ships, trains, and aeroplanes, to substitute petrol and diesel [77,78].

Bio-oil is the main product from the pyrolysis process. Several types of research around the world, in order to maximise and improve the quantity and quality of bio-oil produced, are currently being carried out. Reactor designs are the primary target of researchers to achieve a better-quality bio-oil. As shown in Figure 5, the bio-oil product has a number of applications: it can be improved to be used as a transport fuel or used as a chemical, and it can also be used in turbines and electric power generation engines, or in boilers to generate heat. In summary, the bio-oil product has many applications and deserves large investments in research.

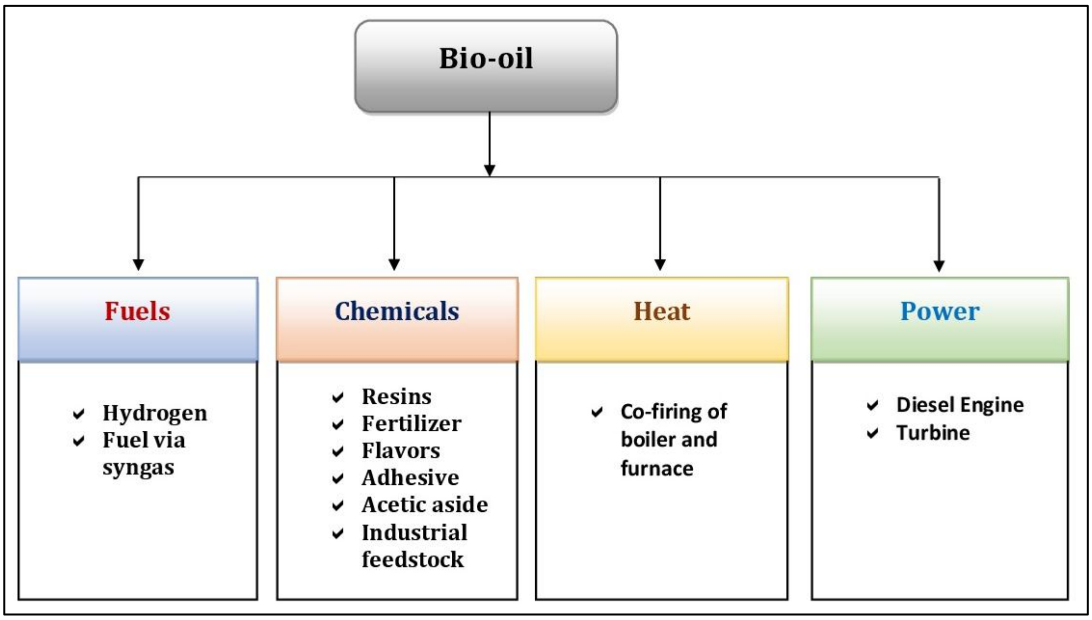

Figure 5. Various applications of pyrolysis bio-oil [77,78].

6.2. Biochar

The production of biochar is an emerging technology which can improve countries' food security and mitigate climate change [79]. In the literature, the potential benefits of applying biochar as soil enrichment have been highlighted heavily, addressing issues such as waste management, bioenergy production, increased soil fertility through alteration of soil pH, retention of nutrients through cation adsorption, reduction of emissions of nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), adsorption of organic pollutants, and improvements in productivity [80]. As a promising modifier to soil, biochar attracts the attention of policymakers in developed countries, such as the United States, Japan, Europe, and some developing countries. Sustainable biochar is one of the few technologies that is relatively cheap, widely applicable, and rapidly scalable. These benefits are confirmed by many investigations [79,81,82], including:

- Reduced nitrogen leaching in groundwater
- Possible reduced emissions of nitrous oxide
- Increased cation exchange capacity resulting in better soil fertility
- Moderation of soil acidity
- Greater water retention
- Increase in the number of beneficial soil microbes

6.3. Syngas

In slow pyrolysis processes, around 10–35% of biogas is produced which is similar to char. Syngas produced from biomass pyrolysis can be used as an alternative renewable source of fuel for industrial combustion processes, as well as for internal combustion (IC) engines. In power generation, transportation, and other sectors, gaseous fuel can be used in converted commercial petrol and diesel engines [83], which was quite common between 1901 and 1920 and, after that, due to the availability of cheap liquid fuels, the usage of gaseous fuels in IC engines. However, in recent years, as the focus has moved towards renewable fuels for engines, the use of syngas in IC engines has, once again, gained interest [84].

Syngas yield is highly influenced by the pyrolysis temperature, and it is possible to achieve a higher yield in flash pyrolysis with high temperatures. He et al. [85] investigated syngas production in a bench-scale downstream fixed-bed reactor from pyrolysis of MSW over a temperature range of 750–900 °C [86]. The researchers used calcined dolomite as a catalyst, and reported a 78.87% gas yield at 900 °C. In another study, Tang and Huang reported 76.64% syngas yield in a radio frequency plasma pyrolysis reactor [87].

Another factor that greatly influences pyrolysis processes and the resulting product distribution is the reactor temperature. With the increase of pyrolysis temperature, the inner moisture of the biomass evaporates first, followed by thermal degradation and devolatilisation of the dried particle portion. Simultaneously, tar is produced, and volatile species are slowly released from the particles' surface, which then undergoes a series of secondary reactions, such as decarboxylation, dehydrogenation, deoxygenation, and cracking, to form components of syngas. Thus, higher temperatures favour tar decomposition and the thermal cracking of tar to increase the proportion of syngas, which reduces oil and char yields [85]. Some researchers have also reported that when the reactor temperature is increased, the syngas flow rate also increases; however, this lasts for a short time, and then dramatically reduces [88].

Syngas mainly consists of hydrogen (H_2) and carbon monoxide (CO). It may also contain a small volume of nitrogen (N_2), water, carbon dioxide (CO_2), hydrocarbons such as C_2H_4, CH_4, C_2H_6, ash, tar, and so on, which depend on biomass feedstock and pyrolysis conditions [89]. These components are obtained during several endothermic reactions at high pyrolysis temperatures.

7. Reactors Employed in the Pyrolysis Process

The heart of the pyrolysis process is the reactor. This is the place where all reactions occur [90–93]. However, to perform flash pyrolysis, it is necessary to have special reactors. For this process, an oxygen-free atmosphere is required in the reactor, and a temperature range between 475 and 550 °C. When the gas flows through the bed, the solid behaves like a liquid [94,95].

The reactor is at the core of any sort of pyrolysis procedure that has been the content of invention, significant research, and advancement, to expand the indispensable physiognomies [96–98]. In the beginning, the developers of the pyrolysis reactor presumed that a minor biomass particle size and very short residence time could obtain prominent bio-oil yields, but further research has found divergent consequences. Component part size and vapour residence time have a slight impact on bio-oil yield, while the parameters significantly trace bio-oil composition [99,100]. The pyrolytic reactor is undoubtedly the most important equipment in the pyrolysis process. Currently, several types of reactors have been designed, most with the aim of maximising the main product of pyrolysis, the bio-oil. There are many pyrolytic reactors used lately, the main ones being those of fluidised bed (bubbling and circulating). Besides these, we also find the fixed bed, jet bed, rotary cylinder, cyclonic reactor, rotary cone, and others. The reactors can be classified into two general systems, either a batch system or a continuous system (continuous flow of biomass occurs, and continuous collection of the products generated). Table 5 shows the comparison of different pyrolysis reactors. The summary of previous research using different reactors and outcomes is listed in Table 6.

Table 5. Comparison of various biomass pyrolysis reactors based on overall performance and efficiency [96].

Pyrolyser	Status (units)	Bio-Oil Yield (wt %)	Operational Complexity	Particle Size	Biomass Variability	Scale-Up	The Inert Gas Flow Rate
Fixed bed	Pilot (single), lab (multiple)	75	Medium	Large	High	Hard	Low
Fluidised bed	Demo (multiple), lab (multiple)	75	Medium	Small	Low	Easy	High
Recirculating bed	Pilot (multiple), lab (multiple)	75	High	Medium	Low	Hard	High
Rotating cone	Demo (single)	70	Medium	Medium	High	Medium	Low
Ablative	Pilot (single), lab (multiple)	75	High	Large	High	Hard	Low
Screw/auger reactor	Pilot (multiple), lab (multiple)	70	Low	Medium	High	Easy	Low
Vacuum	Pilot (single), lab (few)	60	High	Large	Medium	Hard	Low

7.1. Fixed Bed Reactor

The fixed bed pyrolysis system is simple, reliable, and proven for fuels that are relatively uniform in size and have a low content of coal fines which consist of a reactor with a gas cooling and cleaning system, and it was customarily used to produce charcoal [101,102]. The fixed bed reactors generally function with high carbon preservation, low gas velocity, and low residue conveyed over a long solid residence time. A major problem of fixed bed reactors is the formation of tar, although the recent evolution in thermal and catalytic conversion of tar has given feasible opportunities for confiscating tar [103,104]. Figure 6 shows the fixed bed reactor, which is considered simple, and includes the following basic units: drying, granulation, heating, and cooling. In the fixed bed pyrolysis process, the "temperature" ensures that the variables, such as temperature program, heating rates, and residence time in the temperatures, remain within the limits established by the operator and final pyrolysis temperatures between 450 and 750 °C, with heating rates fluctuating between 5 and 100 °C min/min [105].

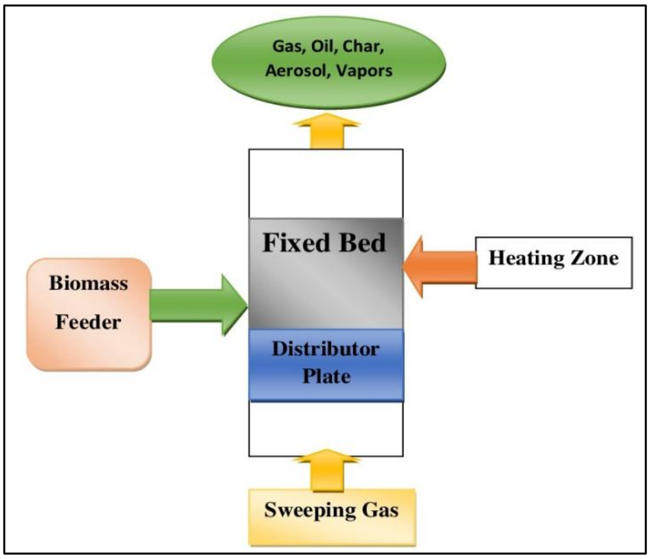

Figure 6. Fixed bed reactor.

7.2. Fluidised Bed Reactor

The fluidised bed reactors (bubbling and circulating) have a well-known technology, and they have a series of industrial applications, where they present themselves as advantageous on a commercial scale, unlike other technologies that are still in the process of improvement [106]. There are several reactors that employ the principle of the fluidised bed, among them, the vortex reactor and the abrasive reactor [105]. Fluidised bed reactors are used in many projects to maximise the liquid product (bio-oil) produced, and several projects demonstrate their real ability to produce good quality bio-oil. As biomass has a very low density, it is common in fluidised bed reactors to use an inert element, usually sand, to give fluid dynamic stability to the process and help biomass heating [107].

The fluidised bed reactor comprises a fluid–solid blend that shows similar properties to the fluid [108]. Fluidised bed reactors seem to be widespread and popular because they offer rapid reaction and heat transfer, a wide and high shallow area of contact between the fluid and solid, and high comparative velocity [108,109]. Different types of fluidised bed reactors are available include bubbling fluidised bed reactors and circulating fluidised bed reactors.

7.2.1. Bubbling Fluidised Beds

Bubbling fluidised bed gasifier is categorised as having high reaction rates, well-understood technology, simple construction and operation, virtuous temperature control, efficient heat transfer to biomass particles, and it has superior lenience to particle size range [110,111]. It is very prevalent, since it generates high quality bio-oil from a dry source. A significant feature of bubble fluidising bed reactors is they require small biomass particle sizes to attain high biomass heating rates [112].

7.2.2. Circulating Fluidised Bed (CFB) Reactors

CFB reactors are comparable with bubbling fluidised bed reactors, and this type of reactor is suitable for large quantities [113]. There are two types of CFB reactors: single circulating and double circulating. The CFB gasifier is considered by all features of the bubbling fluidised bed reactors, along with a higher charge at a lower volume. The CFB pyrolyser is notable for a decent temperature regulator in the reactor [114,115]. Figure 7 shows the circulating fluidised bed reactor.

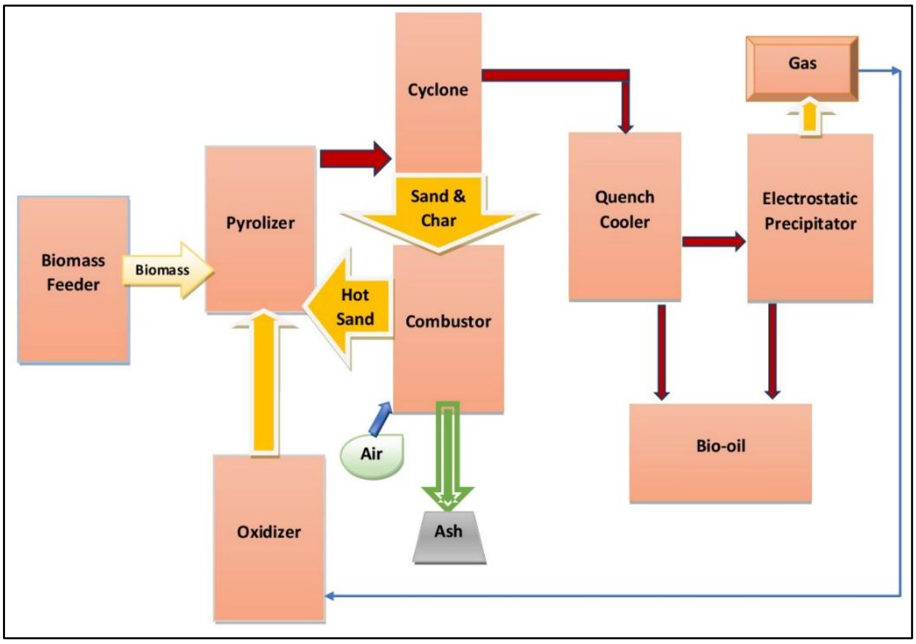

Figure 7. Circulating fluid bed reactor.

7.3. Ablative Reactor

Ablative pyrolysis is primarily dissimilar from fluid bed procedures in the absence of a fluidising gas. Material connected to the wall fundamentally melts, and the residual oil evaporates as pyrolysis vapours. The ablative pyrolysis reactors have good heat transfer with high heating rates and a relatively small contact surface. They also have high energy and cost efficiency, as no heating and cooling of fluidising gases is required, furthermore, they tolerate fixing of condensation units with a small volume in requiring less space at lower costs [116–118].

7.4. Vacuum Pyrolysis Reactor

Vacuum reactors represent a sluggish pyrolysis process with lower heat transfer rates conveyed with the fluidised bed technologies. An induction and burner heater is used with molten salts [80]. For this reactor, the vapours formed are quickly detached from the vacuum. This reactor is categorised by lengthier residence time; it is known to produce larger particles than most fast pyrolysis reactors. There is also no requirement for carrier gas, and the process is mechanically complicated; it needs high investment costs. Consistent operation of vacuum pyrolyser entails a superior feedstock input apparatus which discourages latent investors [116–118].

7.5. Rotating Cone Reactor

The rotating cone reactor is an innovative reactor for flash pyrolysis with tiny char formation. Biomass ingredients, like rice husks, wood, palm kernel, coffee husk, and so on, can be milled in the rotating cone reactor. There is no big scale of commercial implementation for a rotating cone reactor. Nonetheless, high-speed rotation provokes dynamic mixing of biomass that sequentially proceeds to fast heat transfer [114,115,119]. Figure 8 shows the rotating cone reactor.

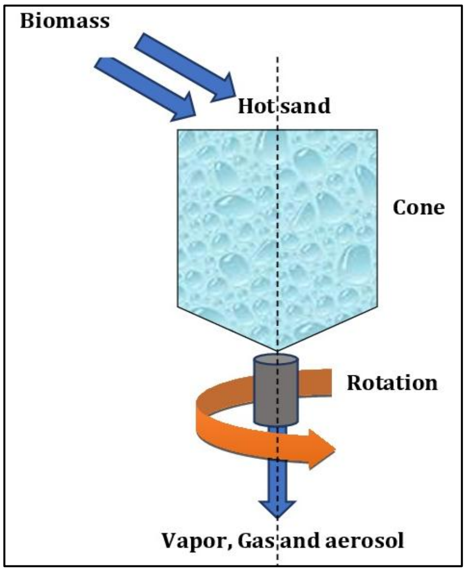

Figure 8. Rotating cone reactor.

Table 6. Summary of previous researches on biomass conversion.

Feedstock	Reactor Type	Temperature (°C)	Yields (wt %)			References
			Char	Bio-Oil	Gas	
Corn stover	Fluidised bed	450–600	28–46	35–50	11–14	[120]
Rice husk	Fluidised bed	450	29	56	15	[121]
Corn cob	Fluidised bed	500	20	62	17	[121]
Sugarcane bagasse	Fluidised bed	500	23	73	4	[122]
Switchgrass	Fluidised bed	480	13	61	11	[123]
Miscanthus	Fluidised bed	505	29	51	12	[124]
Wheat straw	Fluidised bed	550	24	54	24	[125]
Sunflower hulls	Fluidised bed	500	23	57	20	[125]
Rice husk	Fixed bed	100–500	42–48	28–35	-	[126]
Sugarcane bagasse	Vacuum	530	26	51	22	[127]
Rice straw	Vacuum	500	35	47	18	[128]
Douglas fir	Fixed bed	500	22	66	8	[129]
Pine	Vacuum	500	20	50	30	[130]
Wood	Ablative	650	6	60	34	[131]
Barley straw	Ablative	549	32	50	12	[128]
Rice straw	Auger	500	45	26	13	[120]
Hardwood	Auger	500	15	66	18	[132]
Eucalyptus	Conical spouted	500	18	75	6	[133]
Rice husk	Conical spouted	450	26	70	4	[134]
Pine chips	Fixed bed	500	31	15	18	[135]
Softwood	Auger	500	15	69	16	[132]
Olive stone	Rotary kilns	500	26	38	55	[136]

7.6. Auger Reactor

Auger reactors are used to interchange biomass feedstock over an oxygen-free cylindrical tube. In this reactor, vapour residence time could be altered by fluctuating the heated zone. Auger reactors are getting more consideration from many mid-size industries. Challenges for the auger reactor include stirring parts in the hot precinct and temperature transmission on a large scale [114,115]. Figure 9 shows the Auger pyrolysis reactor.

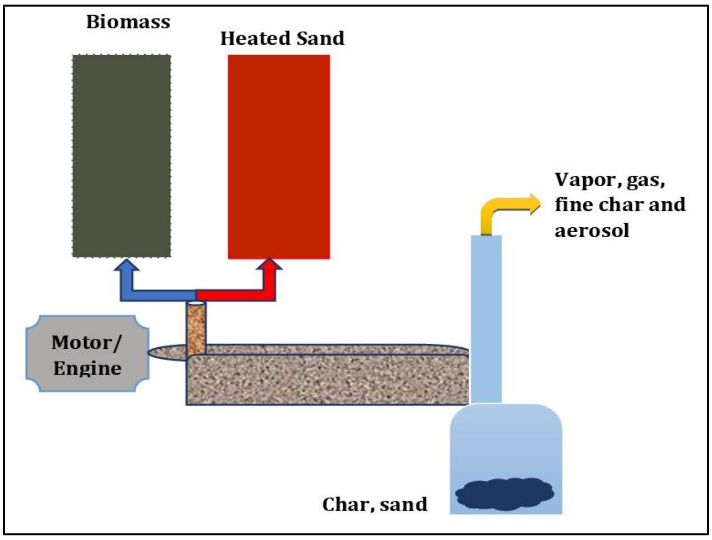

Figure 9. Auger pyrolysis reactor [96].

8. Current Status of Pyrolysis Technology

The deteriorating reserves of fossil fuels have posed a great threat and challenge to the quality of life, the world economy, and the environment [137–139]. Biomass pyrolysis possibly will help reduce CO_2 and the world's dependence on oil production [137,140,141]. These bio-oils have the potential to lower CO_2 discharges; they are derived from plants which use CO_2 for growing. An amalgamation of technologies is required to assimilate reactor design and operational procedure to recover the efficiency of biomass [142,143]. Fast pyrolysis systems process small elements to maximise bio-oil yield, whereas low pyrolysis technologies use wood to produce char chunks [138,139,141]. The recognition of the environmental matters are allied with the use of carbonisation technologies and the technical difficulties of operating fast pyrolysis reactors. Intermediate pyrolysis reactors propose prospects for the extensive balanced production of bio-oil and char [144,145]. Presently, the foremost interests in pyrolysis technology are for CO_2 mitigation, electricity generation from biomass, and energy independence. The pyrolysis technologies can be considered as slow, intermediate, fast, and flash pyrolysis [146–149] but, then again, the most frequently used systems, meanwhile, are the fast and slow pyrolysis processes. Biochar is the key product of the slow pyrolysis, and transpires with moderate temperature, longer residence time, and small heating system rate [150]. Dissimilarly, bio-oil is the key product of fast pyrolysis which formed with a fast heating rate within short residence time [151,152].

Fast pyrolysis produces a higher quality and quantity of bio-oil than the slow pyrolysis [76,153]. It is expected that environmental and economic performance will increase the effectiveness of the pyrolysis process. Various actions are needed to overcome the technical challenges, including plummeting parasitic energy losses, improving pyrolysis reactor outlines, improving feedstock logistics, and enhancing biomass heating rate [9]. Biomass feedstocks are most important to increase the pyrolysis products on a large scale [154,155]. This can be attained by producing energy-condensed products from biomass. Accumulation of metal and ash in reactor bed materials impedes pyrolysis which can reduce bio-oil yields [156,157]. Controlling pyrolysis temperature and heating rate, and using smaller particle sizes can reduce accumulation [158–160]. Recently, a study revealed that an ablative reactor can convert entire wood chips and produce more energy [161,162]. To conclude, cohesive pyrolysis systems that associate gasification or fast pyrolysis are one more important approach for making pyrolysis commercially viable and improving environmental performance [163–167]. Table 7 shows the available pyrolysis plants worldwide.

Table 7. Current pyrolysis plants worldwide [9,168–174].

Reactor Technology	Organisation/Location	Capacity (kg/h)	Desired Product
Fixed bed	Bio-alternative, USA	2000	Char
Bubbling fluidised bed	THEE	500	Gas
	Dyna Motive, Canada	400	Oil
	BEST Energy, Australia	300	Oil
	Wellman, UK	250	Oil
	Union Fenosa, Spain	200	Oil
	Zhejiang University, China	20	Oil
	RTI, Canada	20	Oil
	Waterloo University	3	Oil
	Zhejiang University, China	3	Oil
Circulating fluidised bed	Red Arrow, WI; Ensyn	1700	Chemicals
	Red Arrow, WI; Ensyn	1500	Chemicals
	Ensyn Engineering	30	Oil
	VTT, Finland, Ensyn	20	Oil
Rotating cone	BTG, Netherlands	200	Oil
	University Twente	10	Oil
Vacuum	Pyrovac, Canada	350	Oil
	Laval University	30	Oil
Ablative	PYTEC, Germany	250	Oil
	BBC, Canada	10–15	Char
	PYTEC, Germany	15	Oil
Vortex	Solar energy research Ins.	30	Oil
Another type	Fortum, Finland	350	Oil
	University Zaragoza	100	Gas
	Georgia Tech. Research Ins.	50	Oil

9. Future Challenges

To gain the full potential of biomass pyrolysis technology, such as to enable improved understanding and successful commercialisation, additional research and development are needed. In addition, a couple of issues must be overcome, including the lack of markets for pyrolysis oils and lack of biochar-derived products with well-defined performance characteristics. Also, it is recommended to speed up the improvement and deployment of bio-oil refineries. The improvement of flexible designs for pyrolysis units for producing higher yields of the product is a technical challenge. This review clearly indicates that different pyrolysis technologies have different ranges of product yields. Thus, the selection of pyrolysis technologies, feedstocks, and their operating parameters should be based on the economic trade-offs. However, in addition to the fundamental challenges, a few more important challenges for future biomass pyrolysis research are listed below:

- Understanding the proper working of pyrolysis reactors and processes
- Development of a new reactor that is cost-effective and highly efficient
- Development of catalysts for bio-oil upgrading
- Development of proper solar system reactors
- Post-pyrolysis processing to improve product bio-oil properties
- Understanding the limitations and potential for improvements of the quality of products obtained by biomass pyrolysis
- Development of both fast pyrolysis and bio-oil upgrading, ensuring these are focused on delivering useful and valuable products

For the full implementation of pyrolysis technology, more research is needed to determine designs that will remove oxygen in the gas phase from pyrolysis oil. Pyrolysis technology has the potential to be applied in a vast diversity of situations and, through this process, diversity of products can be obtained. Hence, it is quite difficult to explore a sustainable design for all prospective applications. In addition, balanced financial investments to create new knowledge, technology, and markets for the purpose of building a united vision for the utilisation of pyrolysis technologies is crucial.

10. Conclusions

Biomass is a renewable source for the production of energy which is profusely obtainable globally. The sustainable use of biomass energy can be a supplement for fossil fuels and nuclear energy. Biomass consists of elements, such as carbon, hydrogen, oxygen, and nitrogen. Sulphur is present in smaller proportions, and some types of biomass also contain significant portions of inorganic species. There are several types of pyrolysis processes, namely slow, rapid, ultrafast, and flash pyrolysis which can be used to convert the biomass, which depends upon the process used and also depends on the temperature of the pyrolysis. The main products of the pyrolysis of biomass are bio-oil, biochar, and syngas. The physical and chemical properties of these pyrolysis products depend on the quality of biomass. The bio-oil product has a number of applications; it can be improved to be used as a transport fuel or used as a chemical. Reactor designs are the primary target of researchers to achieve a better-quality bio-oil. For example, fluidised bed reactors are used in many projects to maximise the liquid product (bio-oil) produced, and several projects demonstrate their real ability to produce good quality bio-oil. Auger reactors have the potential to be used in small-scale production. Bio-char is considered as a promising addition to the soil. It can be concluded that the development of biomass pyrolysis technology offers more sustainable products compared to the other available technologies. Finally, in order to gain the full potential of biomass pyrolysis technology and address future challenges, additional research and development are needed.

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Recent Developments in Biomass Pyrolysis for Bio-Fuel Production: Its Potential for Commercial Applications

M.G. RASUL[*] **and M.I. JAHIRUL**
Central Queensland University
Centre for Plant and Water Science, Faculty of Sciences, Engineering and Health
Rockhampton, Queensland 4702, Australia
[*]Corresponding author: m.rasul@cqu.edu.au

Abstract: - There has been an enormous amount of research, in recent years, in the area of thermo-chemical conversion of biomass into bio-fuel (bio-oil, bio-char and bio-gas) through pyrolysis technology due to its several socio-economical advantages as well as an efficient method of conversion compared to other thermo-chemical conversion technologies. However, this technology is still not fully developed with respect to its commercial applications. The current status of pyrolysis technology and its potential for commercial applications for bio-fuel production is discussed in this paper. Aspects of pyrolysis technology which includes pyrolysis principles, types, reactor design, products and their characteristics, economics of bio-fuel production, etc are presented. Advantages and disadvantages of different types of reactors for bio-oil production and their yields, and operating modes of achieving desired products (bio-oil or bio-char or bio-gas) are also discussed and compared. It is found from the literatures that conversion of biomass to bio-fuel has still to overcome a lot of challenges such as understanding of the trade-off between the size of the pyrolysis plant and feedstock, improvement of the reliability of pyrolysis reactors and processes, etc to recommend for commercial applications. A very limited investigation has been done on economical feasibility study of pyrolysis technology. Further study is required for better understanding of the economics, as well as technology, of biomass pyrolysis for bio-fuel production.

Key-Words: - Biomass pyrolysis, bio-fuel production, pyrolysis reactor, cost.

1 Introduction

Current global energy supply is to a large extent based on fossil fuels (oil, natural gas, coal), of which the reserves are finite. Moreover, in order to counter greenhouse gas emissions, the European Union ratified the Kyoto Protocol and emphasised the potential for scientific innovation in 2002, but unfortunately there has been a failure to meet the agreed targets. As a consequence, the global warming situation is likely to be increasing day by day. Atmospheric CO_2 has already exceeded the dangerous level 10 years earlier than had previously been predicted. The award of the 2007 Nobel Peace Prize to the Intergovernmental Panel on Climate Change (IPCC) and to Al Gore establishes the importance of climate change issue. All of these concerns have boosted the importance of research for alternatives to petroleum fuel [1]. Biomass utilisation in mainstream energy uses is receiving great attention due to environmental considerations and the increasing demands of energy worldwide [2, 3]. Combustion of bio-fuel produces less harmful gas emissions such as nitrogen oxides (NOx), sulphur dioxide (SO_2) and soot compared to conventional fossil fuels because biomass contains a small amount of sulphur, nitrogen and ash. In addition, zero or negative carbon dioxide (CO_2) emission is possible from biomass fuel combustion because released CO_2 from the combustion of bio-oil can be recycled into the plant by photosynthesis [4]

Among the biomass to energy conversion through thermo-chemical processes (such as gasification, combustion, pyrolysis, liquefaction, hydrogenation), pyrolysis has attracted more interest in producing liquid fuel product because of its advantages in storage, transport and versatility in application such as combustion engines, boilers, turbines, etc. However it is still at an early stage in development and needs to overcome a number of technical and economic barriers to compete with traditional fossil fuel based techniques [5-6]. The production of bio-fuel (oil, char and gas) by pyrolysis of different biomass species has been extensively investigated in the past; some of these biomass species include wood, bagasse, straws, seedcakes, municipal solid waste (MSW) [7-10], etc. Pyrolysis technology has the capability to produce bio-fuel with high fuel-to-feed ratios. Therefore, pyrolysis has been receiving more attention as an efficient method of converting biomass into bio-fuel during recent decades [11]. The ultimate goal of this technology is to produce high-value bio-oil for competing with and eventually replacing with non-renewable fossil fuels. The development of advanced technologies is the next challenge for pyrolysis researchers to achieve this target [12-13]. Further development of pyrolysis technology is ongoing and many research articles have been published on the pyrolysis concept in in recent times. In this paper, recently published papers are reviewed and discussed. The current status and development of this technology is also presented.

2 Pyrolysis Process Description

Pyrolysis is the thermal decomposition of biomass pyrolysis occurring in the absence of oxygen. More than 5,500 years ago in Southern Europe and the Middle East, pyrolysis technology was used for charcoal production [14]. Pyrolysis has also been used to produce tar for caulking boats and certain embalming agents in ancient Egyptian [15]. Since then, use of pyrolysis processes has been increasing and is widely used for charcoal and coke production. This is because only the burning of charcoal allowed the necessary temperatures to be reached to melt tin with copper to produce bronze.

Biomass preparation is an important factor for smooth operation of pyrolysis because different types of pyrolysis reactors have definite feedstock size limitations for effective heat transfer. For an example, fluidised bed pyrolysis reactors usually require 2-6 mm of particle size. Therefore biomass has to be prepared to the desired size by cutting and grinding operations. In addition to sizing, the biomass materials need to be dried to moisture content below 10 wt% unless a naturally dry material such as straw is available. Drying is essential to avoid adverse effects of water on stability, viscosity, pH, corrosiveness and other liquid properties in the pyrolysis product. By grinding and drying the raw material, the liquid yields can be increased, but at the same time the production costs are increased as well [16]. After drying and grinding, the biomass is fed into the reactor and the pyrolysis process takes place. The char formed in reactor, acts as a vapour cracking catalyst and therefore char removal cyclones are used to separate char from the reactor immediately after pyrolysis. However, some small char particles always pass through the cyclones and are mixed with the liquid product. After solid (char) separation, the vapours and the gases need to be quenched rapidly to avoid continuous cracking of the organic molecules. Quenching of the vapours is usually done with pyrolysis liquid condensers, where the vapours are cooled directly with the bio-oil or a hydrocarbon liquid [17-18].

Pyrolysis reactors have two important requirements for heat transfer: (1) to the reactor heat transfer medium (solid and gas in a fluid bed reactor or the reactor wall in an ablative reactor), (2) from the heat transfer medium to pyrolysis biomass. These heat transfers could be gas-solid where heat is transferred from the hot gas to the pyrolysis biomass particles through convection, and solid-solid where conductive heat transfer occurs. About 90% of heat transfer in fluid bed reactors occurs by conduction, with a small contribution of convection heat transfer of up to 10% because of utilising good solid mixing. Along with convection and conduction, some radiation heat transfer also occurs in all types of reactor. However, several heating methods are used in different pyrolysis reactors to ensure the efficient conversion of biomass into liquid fuel. Some of the methods are shown in Fig. 1 and are listed according to use in reactor types in Table 1.

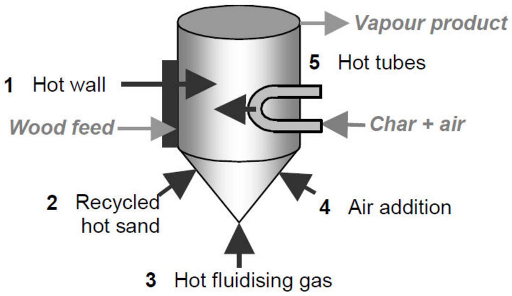

Figure 1: Methods of heat transfer to a pyrolysis reactor [19]

Table 1: Typical heating methods used in different reactors [20-23]

Heating Method	Reactor Type
Heated recycle gas	Bubbling fluidised bed
Wall and sand heating	Circulating fluidised bed
Gasification of char to heat sand	Rotating cone
Direct contract with hot surface	Vacuum
Wall heating	Ablative
Fire tube	Auger
Radio-frequency	Plasma
Electromagnetic	Microwave reactor
Solar	Fluidised bed/Quartz

3 Pyrolysis classification

Depending on the operating condition, pyrolysis can be classified into three main categories:

Conventional, Fast and Flash pyrolysis. Conventional pyrolysis has been used for thousands of years to enhance the char production at low temperatures and low heating rates. However conventional pyrolysis has some technological limitations which made it unlikely to be suitable for good quality bio-oil production. In the fast pyrolysis process, biomass is rapidly heated to a high temperature in the absence of oxygen [19]. The basic characteristics of the fast pyrolysis process are high heat transfer and heating rate, very short vapour residence time, rapid cooling of vapours and aerosol for high bio-oil yield and precision control of reaction temperature [24]. Therefore this technology has received incredible popularity in producing liquid fuels and a range of speciality and commodity chemicals. The flash pyrolysis of biomass is a promising process for the production of solid, liquid and gaseous fuel from biomass which can achieve up to 75% of bio-oil yield [25]. This process can be characterised by rapid devolatilisation in an inert atmosphere, high heating rate of the particles, high reaction temperatures between 450 to 1000 °C and very short gas residence time (less than 1 sec) [26]. However this process has some technological limitations; for instances, Poor thermal stability and corrosiveness of the oil, Solids in the oil, Increase of the viscosity over time by catalytic action of char, Alkali concentrated in the char dissolves in the oil, Production of pyrolytic water [27]. However, the relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters as shown in Table 2.

Table 2: Typical operating parameters and products for pyrolysis process [23, 24-28]

Pyrolysis	Solid Residence Time (s)	Heating Rate (K/s)	Particle Size (mm)	Temp. (K)	Product Yield (%)		
					Oil	Char	Gas
Conventional	450–550	0.1–1	5–50	550–950	30	35	35
Fast	0.5–10	10–200	<1	850–1250	50	20	30
Flash	<0.5	>1000	<0.2	>1050	75	12	13

4 Pyrolysis Products

The three primary products obtained from pyrolysis of biomass are boi-oil, char and gas. However, product yield are well depends on the reaction temperature reported in some recent literature (29-30). This is because different reactions occur at different temperatures in pyrolysis processes. Consequently, at higher temperatures, molecules present in the liquid and residual solid are broken down to produce smaller molecules which enrich the gaseous fraction. Yield of products resulting from biomass pyrolysis can be maximised as follows: (1) charcoal - a low temperature, low heating rate process, (2) liquid products - a low temperature, high heating rate, short gas residence time process, and (3) fuel gas - a high temperature, low heating rate, and long gas residence time process [31]. Table 3 summarises the products created at different pyrolysis conditions. Relative proportions of the end products after pyrolysis of biomass at a range of temperatures are shown in Fig 3.

Table 3: Pyrolysis reactions at different temperatures [32]

Condition	Processes	Products
Below 350 °C	Free radical formation, water elimination and depolymerisation	Formation of carbonyl and carboxyl, CO, CO_2, and charred residue
Between 350 to 450 °C	Breaking of glycosidic linkages of polysaccharide by substitution	Mixture of laevoglucose, anhydrides and oligosaccharides in the form of a tar fraction
Above 450°C	Dehydration, rearrangement and fission of sugar units	Formation of carbonyl compounds such as acetaldehyde, glyoxal and acrolein
Above 500 °C	A mixture of all above processes	A mixture of all above products
Condensation	Unsaturated products condense and cleave to the char	A highly reactive char residue containing trapped free radicals

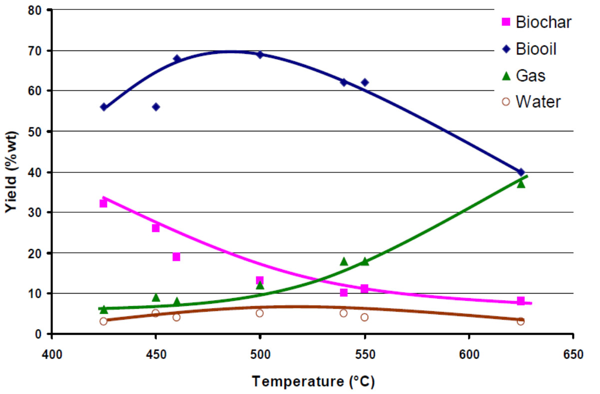

Fig. 2: Relative proportions of end products in pyrolysis of biomass [32]

4.1. Pyrolysis bio-oil

Pyrolysis bio-oil is the liquid produced from the condensation of vapour of a pyrolysis reaction. The pyrolysis bio-oils have heating values of 40-50% of that of petroleum fuels. The main advantages of pyrolysis liquid fuels includes [28, 33]:

- CO_2 balance is clearly positive in biomass fuel.
- Possibility of utilisation in small-scale power generation systems as well as use in large power stations.
- Storability and transportability of liquid fuel.
- High-energy density compared to biomass gasification fuel.
- Potential of using pyrolysis liquid in existing power plants.

Pyrolysis bio-oils are composed of a complex mixture of about 300 to 400 oxygenated compounds. During storage, the pyrolysis oil becomes more viscous due to chemical and physical changes as many reactions continue and volatiles are lost due to aging. Studies found that the reactions and aging effects occur faster at higher temperatures but the effects can be reduced if the pyrolysis oil is stored in a cool place [34-35]. However, numerous unknown compounds and factors are affecting the thermo-physical properties of pyrolysis bio-oil. It has limitations in fuel quality, phase separation, stability, fouling issues on thermal processing and economic viability of pyrolysis bio-oil. Some physical properties and characteristics of pyrolysis bio-oil are described in Table 4. Fahmi *et. al.* (2008) concluded that more stable pyrolysis oil can be produced if an energy crop is used [38]. However, this would affect the yield by lowering the organic yield due to the high level of ash/metal content and producing a high level of reaction water, resulting in a reduction of the heating value of the oil as well as risking phase separation. The results of this would imply further investigation is necessary on a trade-off analysis between yield and oil stability. However, feedstock content limits for metals, ash and lignin also need to be identified and addressed in order to produce bio-oil which can be used for commercial applications, which does not change considerably over time, but is still produced at acceptable yield levels and with good heating values.

Shihadeh and Hochgreb (2000) found that thermal efficiency of pyrolysis oils is identical to that of diesel fuel in combustion engine operations, but they exhibited excessive ignition delay [39]. Therefore pyrolysis oil requires a moderate degree of preheated combustion air for reliable ignition. However the pyrolysis oil yields, quality and stability can also be modified by process variables such as heating rate, pyrolysis temperature and residence times [40]. Other factors such as different reactors, particle size and char accumulation can affect the yield and quality of the pyrolysis oil by varying its ash content and composition which affects the thermal degradation of these biomass. Until now there is no comprehensive study to minimise these effects. Therefore further research is required, in order to obtain an overall picture of thermochemical conversion processes to produce high quality pyrolysis oil.

Table 4: Physical properties and characteristics of pyrolysis bio-oil [36-37]

Properties	Oil Characteristics	Reasons
Appearance	Dark red-brown to dark green	Micro-carbon and chemical composition
Odour	Distinctive odour – an acrid smoky smell	Lower molecular weight ofaldehydes and acids
Density	Very high compared to fossil fuel • Pyrolysis bio-oil: 1.2 kg/litre • Fossil oil: 0.85 kg/litre	High moisture and heavy molecule contamination
Viscosity	Can vary from as low as 25 centistokes (cSt) to as high as 1000 cSt	Wide range of feedstock, water content and the amount of light ends collected
Heating value	Significantly lower than fossil oil	High oxygen content
Aging	Viscosity increase, volatility decrease, phase separation and deposition of gum occur with time	Complex structure and high pH value
Miscibility	Miscible with polar solvent but totally immiscible with petroleum fuel	Polar in nature

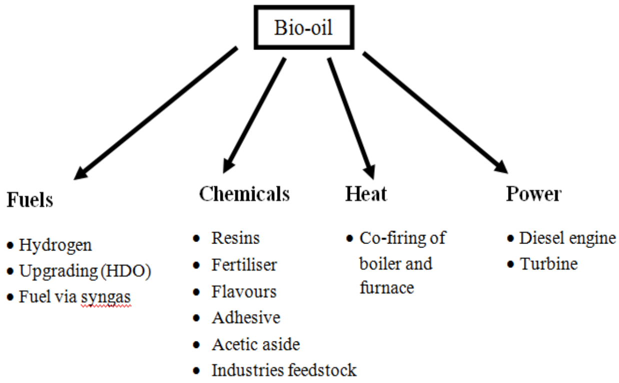

Fig 3: Various applications of pyrolysis bio-oil [41]

Pyrolysis bio-oil presents a much better opportunity for high efficiency energy production compared to traditional biomass fuel such as black liquor or hog oil. Therefore a significant effort has been spent on research and development directed to the application of bio-oil for the generation of heat and power and for use as a transport fuel. Unfortunately bio-oils have not reached commercial standards yet due to significant problems during its use as fuel in standard equipment such as boilers, engines and gas turbines constructed for operation with petroleum-derived fuels. The main reasons for this are poor volatility, high viscosity, coking, and corrosiveness of bio-oil. Bio-oil can be used as a substitute for fossil fuels to generate heat, power and chemicals. Short-term applications are boilers and furnaces (including power stations), whereas turbines and diesel engines may become users in the somewhat longer term (Fig 3). Upgrading bio-oil to a transportation fuel quality is technically feasible, but needs further development. Transportation fuels such as methanol and Fischer-Tropsch fuels can be derived from bio-oil through synthesis gas processes. Furthermore, there is a wide range of chemicals that can be extracted from bio-oil.

4.2. Bio-char from pyrolysis

Depending on the biomass and pyrolysis conditions, 10 to 35% bio-char is produced. Rocha *et al.* (2002) carried out an investigation to demonstrate bio-char yield variation for different temperature regions in a fluidised bed pyrolysis reactor [42]. In their investigation, three different temperature regions were found to produce different bio-char yields during pyrolysis (Fig. 4). At a low temperature (450 - 500°C) zone, bio-char quantity was high due to low devolatilisation rates and low carbon conversion. In a second moderate temperature (550 - 650°C) zone, the production of bio-char was reduced dramatically. The maximum yield in this region was found to be about 8 to 10% of bio-char. In the high temperature (over 650°C) zone, bio-char yield was very low.

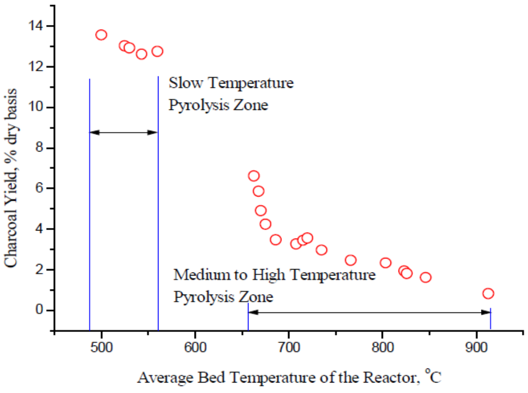

Fig 4: Charcoal (or bio-char) yields variation versus average temperature in the fluidised bed [42]

Bio-char physical characteristics are greatly affected by the pyrolysis conditions such as reactor type and shape, biomass type and drying treatment, feedstock particle size, chemical activation, heating rate, residence time, pressure, flow rate of inert gas, etc [43-48]. For example, pyrolysis operating conditions like higher heating rate (up to 105-500°C/sec), shorter residence time and finer feedstock produce finer bio-char whereas slow pyrolysis with larger feedstock particle size results in a coarser bio-char. Moreover, wood-based biomass generally produces coarser bio-char. On the other hand, crop residues and manures generate a process in which particles of biomass rub against the wall of a heated tube as they degrade; therefore this process is limited by the rate of heat supplied to the reactor. On the other hand the rate of heat absorption by the particles is better compared with fluid bed reactors. That means that larger biomass can be more practically processed by ablative reactors. A comprehensive study on advantages and limitations of different types of pyrolysis reactors has been conducted in this study and presented in Table 12. According to the findings of this study, the recommendations to achieve desired outputs from pyrolysis have been shown in Table 13.

4.3. Syngas

Syngas mainly consists of hydrogen (H_2) and carbon monoxide (CO). It also contain small amount of carbon dioxide (CO_2), water, nitrogen (N_2), hydrocarbons such as CH_4, C_2H_4, C_2H_6, tar, ash, etc., depending on biomass feedstock and pyrolysis conditions [49-52]. These components are obtained during several endothermic reactions at high pyrolysis temperatures. H_2 is produced from the cracking of hydrocarbons at higher temperatures. CO and CO_2 are the indicators of the presence of oxygen in the biomass. Those components mainly originate from the cracking of partially oxygenated organic compounds. Therefore, as a highly oxygenated polymer, the amount of cellulose present in the biomass is an important factor determining the amount of carbon oxides produced [53-54]. The light hydrocarbons such as CH_4, C_2H_4, C_2H_6 etc may be due to the reforming and cracking of heavier hydrocarbons and tar in the vapour phase [55]. However, the composition of syngas is clearly affected by the reactor temperature as shown in Fig. 5. H_2 and CO increases sharply with the increase of the temperature while other components show an opposite tendency. The molar ratio of H_2 and CO in syngas is an important factor that determines its possible applications. For example, a higher H_2/CO molar ratio is desirable to produce Fisher-Tropsh synthesis for the production of transportation fuel and to produce hydrogen for ammonia synthesis [56], so optimisation of reaction temperature in pyrolysis is a critical issue for syngas production.

Syngas from biomass pyrolysis could be a renewable alternative fuel for internal combustion (IC) engines and industrial combustion processes. Commercial petrol and diesel engines can be easily converted to use gaseous fuel for the use of power generation, transportation and other applications [58-61]. However many commercial gaseous fuel IC engines were used between 1901 and 1920. After then the trend declined due to available cheap liquid fuels. Recently interest has again developed in the use of syngas in IC engines due to the emergence of the need for renewable fuel engines.

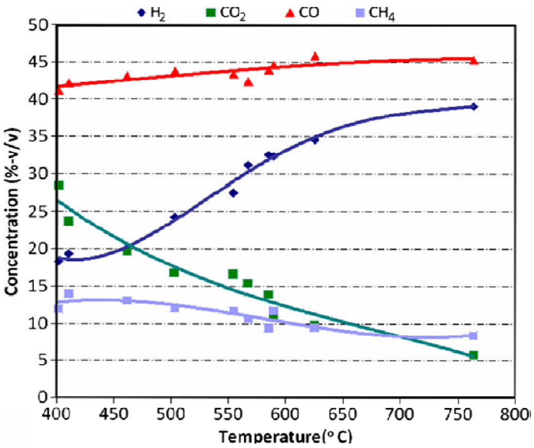

Fig 5: Gas composition of pyrolysis of cotton stalks versus pyrolysis temperature [57]

5 Pyrolysis Reactors

The reactor is the heart of any pyrolysis process. Reactors have been the subject of considerable research, innovation and development to improve the essential characteristics of high heating rates, moderate temperatures and short vapour product residence times for liquids. At first, pyrolysis reactor developers had assumed that small biomass particles size (less than 1 mm) and very short residence time would achieve high bio-oil yield, however later research has found different results. Particle size and vapour residence time have little effect on bio-oil yield, whereas those parameters greatly affect bio-oil composition [62-63]. With the continuation of pyrolysis technology development, a number of reactor designs have been explored to optimise the pyrolysis performance and to produce high quality bio-oil. Among the developed pyrolysis reactors, fluidised bed reactors are most commonly used, followed by rotating cone, vacuum, ablative, vortex etc. However all types of reactor have technological advantages and limitations compared with each other. For an example, ablative pyrolysis is a process in which particles of biomass rub against the wall of a heated tube as they degrade; therefore this process is limited by the rate of heat supplied to the reactor. On the other hand the rate of heat absorption by the particles is better compared with fluid bed reactors. That means larger biomass can be more practically processed by ablative reactors. A comprehensive study on advantages and limitations of different types of pyrolysis reactors has been conducted in this study and presented in Table 5. According to the findings of this study, the recommendations to achieve desired outputs from pyrolysis have been shown in Table 6.

6 Energy Consumption in Pyrolysis

Large amounts of thermal energy are needed to maintain suitable pyrolysis temperatures in the reactor wall or heat carrier. Energy is also needed for grinding and drying the feed material into a usable particle size. Numerous electric motors are required to provide the work to achieve the different flow rates, pressures and power the filtration systems. Therefore, energy efficiency is an important measure for identifying the performance of a pyrolysis process which can be expressed as follows:

$$\eta_{energy} = \frac{E_{bio-fuel}}{E_{feedstock} + E_{Pyrolysis}} \text{ .... (1)}$$

Where, η_{energy} is the process energy efficiency; $E_{bio-oil}$ is the energy content in the product bio-fuel; $E_{feedstock}$ is the energy content in the biomass feedstock and $E_{pyrolysis}$ is the external energy consumption in the pyrolysis process. In general, the three components can be considered in the calculation of energy consumption for pyrolysis as follows:

$$E_{Pyrolysis} = E_{Drying} + E_{Target} + E_{Reaction} \dots (2)$$

The first component (E_{Drying}) of energy involves dewatering the wet biomass to dry biomass. The second component (E_{Target}) of energy is used to heat dried biomass to the pyrolysis temperature, and the third component ($E_{Reaction}$) of energy is consumed to decompose the biomass during the pyrolysis reaction.

Bramer and Holthuis [71] conducted a study to find energy required to run a small scale (30 kg/h biomass) pyrolysis system using a PyRos reactor. This study concluded that about 5.48% of produced energy is sufficient for the energy need for running the pyrolysis process.

Table 5: Advantages, disadvantages and bio-oil yield of different pyrolysis reactors [64-70]

Reactor type	Advantages	Limitations	Oil Yield
Fixed bed	• Simple design • Reliable • Biomass size independent	• Long solid residence time • Difficult to remove char	35-50%
Bubbling fluidised bed	• Simple design • Easy operation • Suitable for large scale	• Small particle sizes are needed	70-75%
Circulating fluidised bed	• Well-understood technology • Good control • Large particle sizes can be used	• Suitable for small scale • Complex hydrodynamics • Char is finer	70-75%
Rotating cone	• No carrier gas required • Less wear	• Complex process • Small particle • Small scale	65%
Vacuum	• Produces clean oil • Can process larger particles of 3-5cm • No carrier gas required • Lower temperature required • Easier liquid condensation	• Slow process • Solid residence time is too high • Require large scale equipment • Poor heat and mass transfer rate • Generates more water	35-50%
Ablative	• Inert gas is not required • Large particle sizes can be processed	• Reactor is costly • Low reaction rate • Low reaction rate	70%
Auger	• Compact • No carrier gas required • Lower process temperature	• Moving parts in hot zone • Heat transfer is suitable for small scale	30-50%
PyRos	• Compact and low cost • High heat transfer • Short gas residence time	• Complex design • High impurities in the oil • High temperature required	70-75%
Plasma	• High energy density • High heat transfer • High temperature • Very good control	• High electrical power consumption • High operating costs • Small particle sizes required	30-40%
Microwave	Compact • High heating rate • Large size biomass can be processed • Uniform temperature distribution • High temperature	• High electrical power consumption • High operating costs	60-70%
Solar	• Use renewable energy • High heating rate • High temperature	• High costs • Weather dependant	40-60%

This energy can be obtained by combusting one of the two by-products - the bio-char, or all the produced gas with a small proportion of the bio-char. Moreover, fraction of energy recovery from biomass can also be good measure to determining the effectiveness of biomass pyrolysis which is the ratio of energy available in the products and energy containing in biomass. Stals *et. al.* [72] has conducted such an analysis and achieved 35 – 39 percent energy recovery in flash pyrolysis of different hardwoods. However the results presented in these studies are not enough to make a final conclusion regarding the energy efficiency of industrial scale pyrolysis plants. In order to obtain a clear energy picture and hence improve the energy efficiency, a comprehensive energy audit should be conducted in an industrial scale pyrolysis plant.

Table 6: Recommended pyrolysis technology according to product

Product		Pyrolysis Type	Reactor	Heating Method	Temp (°C)	Biomass
Bio-char		Conven.	Fixed bed	Furnace or kilns	< 300	Walnut shell, olive husk, hazelnut shell
Bio-oil	Large scale	Fast	Bubbling fluidised bed	Heated recycle gas	450 – 550	Agriculture residue, wood chip, fruit shell
	Medium scale	Fast	Circulating fluidised bed	Wall and sand heating	450 – 550	Forest residue, municipal waste, dry wood, waste tyres
	Small scale	Flash	PyRos	PyRos heating	450 – 550	Grass, husk, wood dust
Syngas		Conven./ Fast	Microwave	Electromagnetic	>800	Rice husk, wood dust

7 Pyrolysis Economics

Economic viability is the key factor in the development of commercial pyrolysis processes. Currently, pyrolysis products are unable to compete economically with fossil fuels due to high production costs. The pyrolysis technology has to overcome a number of technical and non-technical barriers before industry can implement their commercialisation and usage [73]. Production cost of pyrolysis product is quite high compared to production of fossil fuel. The main component of pyrolysis plants are the reactor, although it represents only 10-15% of the total capital cost. The rest of the cost consists of biomass collection, storage and handling, biomass cutting, dying and grinding, product collection and storage, etc.

The cost of a pyrolysis production plant could be classified into two main categories: capital investment, and operating or variable costs. Capital or fixed cost includes: pyrolysis module, basic equipments, feed handling and storage, and development of facilities (land, road, transport, building etc). The fixed cost is primarily depends on the technology, plant size and biomass feedstock. Variable costs include biomass harvesting or feedstock, maintanance, product transport, labour, utility, transport etc. The percentage approximate contributions of different components on variable cost are shown in table 7.

Table 7: Variable cost for pyrolysis plant [74]

Items	Percentages
Biomass harvesting or feedstock	23 – 30%
Maintenance	17 – 24%
Utilities	22 - 25%
Labour	12 – 19%
Grinding	7 – 9%
Transportation	5 - 7%

Several factors are associated with the cost of biomass pyrolysis energy conversion which includes process technology, the scale of operation, feedstock, year of construction, and so on. Moreover, scale-up is an increasingly important issue as pilot and demonstration plants have to be commercially realized. With analyzing the impact of economic on the scale of pyrolysis plant, Arbogast *et. al.* (2012) conclude that competitive economic bio-oil production can be achieved by large scale production. It can also be attained dominate the economics of the value chain and the financial risk associated with initial individual investment [75]. A techno-economical study on four different sized fast pyrolysis plant using four different technologies has been conducted by Polagye *et. al.* [76]. This study included mobile, transportable, stationary and re-locatable plant sized 10, 100, 1653 and 500 ton per day respectively and showed a good correlation between plant size, technology and different types of cost.

Similar analysis has been conducted by Islam and Ani [76] for converting rice husk waste to pyrolysis oil and solid char. Three different-scaled fluidised bed reactors, of feed throughput 0.3, 100, and 100 kg/h, were assessed in this study. Those studies concluded that the grater the plant size and lower the unit product cost and hence more economically suitable where as small plant dramatically increase the production cost. While analysing bio-oil production curve in Fig. 6, this statement become more obvious. Therefore an economically attractive operation requires low cost feed, large scale operation and technical development to improve performance and reduce costs.

8 Future challenges

Different applications of pyrolysis bio-oil are complex which is unlikely to be technically and economically feasible today. To achieve the potential of pyrolysis technology for bio-fuel production from biomass, additional research and development are needed. Despite rapid development over the last few decades, commercialisation of pyrolysis bio-oil technology is still a long way off and needs to overcome many techno-economic barriers. Some of the important challenges for future pyrolysis research are listed below:

- Understand the trade-off between the size of the pyrolysis plant and feedstock and transportation costs to a centralized upgrading facility.
- Understand the limitations of the processes and where improvements can be made.
- Improvement of the reliability of pyrolysis reactors and processes.
- Identify norms and quality standards of pyrolysis bio-oil for producers and users.
- Undertake in-depth life cycle energy and economic analyses of integrated pyrolysis plants
- Encourage implementation processes and applications of pyrolysis products.
- Determine detailed characteristics of upgraded oil and other products.
- Development of more efficient technologies for the production of chemicals and biofuels from pyrolysis oils.

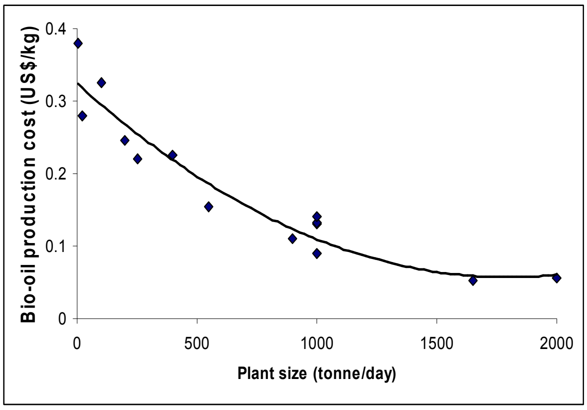

Fig 6: Bio-oil production cost with plant size [74, 77-84]

Conclusions

Much attention has been given to biomass pyrolysis because of an opportunity for the processing of agricultural residues, wood wastes and municipal solid waste into clean energy. This study identified the route of pyrolysis technology i.e., selection of operating modes of pyrolysis, types of reactor, etc., based on the desired product output (bio-oil, bio-char or syngas). However, a sound understanding of the inherent process will allow pyrolysis products to be maximised.

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