Review on Process Development and Challenges in Biomass Pyrolysis

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Abstract: In recent times, the escalation of greenhouse gases, air pollution and depletion of the ozone layer has enforced the researchers to renovate the regular use of fossil fuels into alternate methods which are non-toxic, eco-friendly, and cost-effective. Biomass is one of the traditions to swap fossil fuels. Biomass can be transmogrified into beneficial and eco-friendly forms of energy under various conversion processes. The obtained energy can be used for heating water, industrial heating process, and generating electricity. Pyrolysis is a method to alter biomass into useful products, as the final yields of this process include bio-oil, char, methane (CH₄), hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂). It is well known for its high efficiency and environmental performance. In this method even the agricultural residues, waste woods, solid municipal waste, plant wastes can be utilized. This review comprehends the various concepts on products of biomass pyrolysis, mechanisms, and several pre-treatment processes used for efficient pyrolysis of biomass have been analysed. The impact of various fundamental constraints such as temperature, heating rate, particle size was studied and their influence on yield and composition were studied.

Keywords – Biomass, Pyrolysis, Eco-friendly, Catalyst, Bioreactors

1. Introduction

For sustainable development of any nation, well-organized use of energy plays a vital role. With the need for global energy supply, fossil fuels which are a finite source of energy cannot serve for all requirements. [1] There is need to abate the use of fossil fuels and accrue the development and research in alternate sources of energy. The utilization of petroleum fuels increases the number of toxic emissions such as carbon dioxide (CO₂), carbon monoxide (CO), and emissions of sulphur oxides (Sox) and nitrous oxides (NOx).[2] The requirement for the current century is direct replacement of these fossil fuels to reduce the emissions of pollutants and the continuous depletion of it. The future energy consumption and sustainability and distribution of energy must be planned and managed by all nations to reduce the amount of toxic and harmful products into the atmosphere. These conventional fuels such as coal, oil and natural gas can be replaced with biomass, as it is renewable and unharmful to the environment.[3]
There are several methods for producing clean and non-renewable energy for meeting the current demands. Biofuels is one potential form of energy which can meet the energy demands required for the current situation. Moreover, biomass produces very less emissions of NOx and Sox compared to conventional fossil fuels because of its carbon-neutral composition. Pyrolysis has been increasingly popular due to its better quality compared to other forms of biomass conversions. Biomass pyrolysis is inexpensive, reduces the number of landfills, better produce of bio-oil and reduces emissions of greenhouse gases. One advantage of pyrolysis method is that it can be operated at atmospheric temperatures.
2. Various Pre-treatment Processes

In order to enhance the products of pyrolysis and increase the efficiency, the biomass needs to undergo some pre-treatment processes. This is done by disrupting the lignocellulosic structure. The 3 main pre-treatment processes are physical pre-treatment, chemical pre-treatment, thermal pre-treatment and biological pre-treatment processes.[14] These processes have been discussed in this section.

2.1 Physical Pre-treatment Processes

The temperature gradient inside the reactor influences the product produced and the efficiency of the biomass pyrolysis.[15] If the size of the particle is larger, then char is produced in higher quantity. Cost of operation increases with the intensification in the particle size of biomass. Hence, it is vital to select the appropriate particle size.

2.1.1 Influence of Particle Size

The bigger particles can result in more formation of char and pyrolytic gases than efficient bio-oil. But if the particle size is too large, then it can lead to the decrease in the efficiency of pyrolysis. When size of the biomass particles is large, it ameliorates the amount of water produces by the rise in the particle size. Also, production of gases like Carbon monoxide (CO) and carbon dioxide (CO₂) increases. [16]

2.1.2 Densification

Apart from the size of the particles, the density if the biomass also plays a crucial role in deriving the required products. General methods for biomass densification are pellet mill, cuber, briquette press, screw extruder, tabletizer, and agglomerator. By compacting biomass more yield can be achieved. [17]

2.2 Chemical Pre-treatment Processes

The structure of biomass is rigid and has high mechanical strength. The use of chemicals can influence these inorganic minerals to change their properties and hence, enhance the efficiency of pyrolysis. Some of the common chemical pre-treatment methods used are acid pre-treatment, hydrothermal pre-treatment and steam explosives.[18]
2.3. Thermal Pre-treatment Processes
Thermal pre-treatment is done to reduce the amount of water in the biomass. The drying up of the biomass can conserve some energy. The amount of energy required for increasing the feedstock temperature for better ramping rate is thereby reduced. This treatment is beneficial only to attain bio-oils from biomass pyrolysis. To produce char form pyrolysis more amount of water is required.[20]

2.4. Biological Pre-treatment Processes
It is an environmentally friendly method. In this method, rotten fungi are used to decompose the components of the biomass. This makes the process of pyrolysis easy and simple. Different types of rot fungi are used. Some of the fungi used are white, brown and soft rot fungi which mainly degrade the composition of lignin in the biomass. Different types of rot fungi produce different effects on the pyrolysis of biomass. The toxic emissions such as Sox and NOx are reduced by using rot fungi.[21,22]

3. Effects of reaction conditions

3.1 Reaction to Atmosphere
Pyrolysis of biomass is always carried out in inert atmosphere. Some gases can be used as carrier gas in pyrolysis such as N2, H2, CO, CO2, CH4 and steam. Steam has comparatively more advantage than others since it can increase the yield of Bio-oil through to decreasing the secondary cracking reactions rates.[23] Therefore, carrier gas has influence over products yield, functional groups in the products, energy content of the Bio-oil and etc. This results in the change of mechanism in the pyrolysis reaction. For example, in one research different carrier gases including N2, CO, CO2, CH4 and H2 were used for pyrolysis of biomass in a fluidised bed reactor. The result indicated that CH4 and CO produced the highest (58.7 wt.%) and lowest (49.6 wt.%) bio-oil yields, respectively [24,25].

3.2 Temperature
During Pyrolysis, Decomposition of biomass undergoes various stages. The first stage proceeds with internal rearrangement like water elimination, bond breakage, appearance of free radical’s formation of carbonyl, carboxyl and hydro peroxide groups takes place at 122–202 °C. The Second stage involves pyrolysis production including char, bio-oil and gases start to form at 200-600°C.[26,27] The third stage is the stagnant decomposition of char and therefore carbon rich residual solids are formed at >600°C. At stage four, >600°C Dehydration and Decarboxylation reactions takes place resulting in increase of aromatic compounds, contents of the polar and aliphatic. [28,29] The yield level of gases changes as well. The temperature also affects the water content. At the temperature up to 360 °C, the production of water increased while the further increase of temperature did not result to increase of water production. Whereas, from 580 °C the water production starts to decrease.[30]
3.3 Heating Rate
The Heating rate of biomass particles plays a crucial role in differing slow pyrolysis and fast pyrolysis. Slow pyrolysis requires a heating range of 1-100°C/min. Fast pyrolysis requires a heating range of >1000°C/min. [32] Increasing heating rate could help in Depolymerisation of cellulose, Hemicellulose and it minimises the residence time of the volatiles inside the reactor and also secondary reactions. It promotes cracking reactions and produced more volatiles and less char. [33] Higher heating rates result in decreases of water content in the bio-oil due to volatile dehydration. It also produces char with smaller pore volume and promotes the increase of CO and CO2. On Other Hand, Lower heating rate rates will increase intra-chain hydrogen bonds of cellulose functional groups, enhancing the probability of collision to produce a dehydration reaction. [34]

4. Catalytic Pyrolysis
The bio-oil derived from the pyrolysis cannot be directly used in engines as a fuel. The derived bio-oil must be added with a catalyst to increase the effectiveness. There are various methods to improve the quality of fuel of bio-oil with lower oxygen content. Catalysts are directly added in the pyrolysis step to remove the oxygen in oxygenates as fast catalyst deactivation ca prevent their use and be expensive. The production of the yield can be improved under the presence of catalyst. [35]
4.1. Use of Zeolite as catalysts
Zeolites are generally used as catalysts for biomass pyrolysis. ZSM-5, Y zeolite, Beta zeolite, MCM-41, CM-22, Mordenite, SAPO-34 are some of the common zeolitic catalysts used. The use of zeolite catalysts upsurges aromatic yields and formation of coke. If catalysts have bigger pore sizes, then it favours the formation of coke. [37,38] The size of the pores of the catalysts is also one of the factors affecting the yield. Both zeolite and non-zeolite catalysts depend on the preference of the yield. However, the use of zeolite catalysts causes more formation of coke and rapid deactivation of the catalysts. If the bio-oil is the desirable yield, then use of zeolite catalysts is not preferred as it is more expensive and lesser quality of bio-oil are produced. [39,40]

4.2. Non-zeolite as catalysts
There are various zeolitic catalysts used for pyrolysis in biomass. Major components include oxides of metal, noble gases, and transition metals. Usually, Na2CO3 and Al2O3 are used as non-zeolite catalysts for biomass pyrolysis.[42,43] This results in the instability of the bio-oil yielded from the biomass pyrolysis. But with the presence of metals such as Platinum (Pt). Use of two catalysts Pt/Al2O3 and Na2CO3/Al2O3 showed that the instability in the biomass was improved. [44]

5. Results and Discussion
A reactor is the crux of the process of pyrolysis. The characteristics and parameters of the reactors, heating rate, temperatures, time of residence all influence the products of pyrolysis. There has been continuous research and development to increase the efficiency and yield in reactors of various products of biomass pyrolysis. [44, 45] The following table 1, depicts the applications, advantages, disadvantages, and percentage of yield for each reactor type.

There are several pre-treatment processes in biomass pyrolysis. Selection of pre-treatment also depends on the installation cost, transportation facilities, product required, quality of product and production rate. [48,49] Several processes such as biological, physical and chemical treatment are available. The best methods of pyrolysis are listed in table 2 along with the justification.
Table 1. Ranking for different types of reactors and their justifications [46,47]

| RANK | TYPE                         | YIELD (%) | JUSTIFICATION                                                                                                                                 |
|------|------------------------------|-----------|---------------------------------------------------------------------------------------------------------------------------------------------|
| 01.  | Bubbling Fluidized Bed Reactor | 70-75     | It is selected as the most preferred method due to its ease of operation and excellent temperature control. Moreover, it is suitable for large scale production. |
| 02.  | Circulating Fluidized Bed Reactor | 70-75     | Even though it has the same percentage of yield, this reactor has some defects due to its complexity in hydrodynamics and unlikely for large scale production. |
| 03.  | PyRos Reactor                | 70-75     | This reactor has a complicated design and requires high time of residence. It required high rate of temperature to carry on the process.              |
| 04.  | Ablative Reactor             | 70        | Eliminates the need for high temperature and inert gas. This reactor can work with larger particles. It has the limitation for lesser reaction rate.        |
| 05.  | Microwave Reactor            | 60-70     | This reactor is known for its efficient control and compact size. It can process large particles and require high temperature. This requires high electricity consumption. |
| 06.  | Rotating Cone Reactor        | 65        | Wear of the materials inside the reactor is less, but this method cannot be used for large scale production. Heated movement is used to control the parts. |
| 07.  | Solar Reactor                | 60        | Does not have any harmful effect on the environment. This is a suitable method only for small scale production. But this reactor depends on weather. |
| 08.  | Fixed Bed Reactor            | 35 – 50   | Char produced is difficult to remove. Conservation of carbon is high, anyway due to its simple design and size independent nature of particle it is preferred. |
| 09.  | Vacuum Reactor               | 35 - 50   | Good for cleaner yields of bio-oil. But this is a very slow process. Time for residence is time & heat transfer is low. Requires equipment for removing the water produced. |
| 10.  | Auger Reactor                | 30 - 50   | Carrier gas is not required. Wear and tear of parts are high due to high temperature in the reactor. Not recommended for large scale production. |

Table 2. Best Pre-treatment process for biomass pyrolysis [50]

| RANK | PRE-TREATMENT PROCESS | JUSTIFICATION                                                                                                                                 |
|------|-----------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| 01.  | Torrefaction          | Electricity required is less, maintenance cost is low, easy to transport biomass, energy gained is more. Hemicellulose can be easily decomposed. |
| 02.  | Drying                | Percentage of bio-oil yield is high in drying, does not require further process to remove excess water. Mass of biomass is reduced by drying.     |
| 03.  | Acid/Alkali Pre-treatment | Compared to concentrated acids, toxic material produced are less. Rate of recovery of sugar from lignin and hemi-cellulose are high.              |
| 04.  | Densification         | Storing and transportation cost are less. Energy density is high but requires high cost.                                                  |
| 05.  | Concentrated Acid     | Effects of concentrated acid is harmful and toxic for environment. Sometimes, it can corrode other materials in the reactor. Concentrated acids require high-cost licensing. |
| 06.  | Biological treatment  | Very slow rate process, cannot be implied for large scale production, requires mild environmental conditions and low rate of treatment.       |
6. Conclusion

Uprising need and demand for the requirements and necessities for energy is upsurging at high rates. This rise in demand clearly shows that there must be distributed source for energy. Humanity cannot solely depend on fossil fuels to meet the daily demands. Moreover, to move to a safer and cleaner form of energy, renewable energy is much appreciated. This review paper depicts on such method, that is biomass pyrolysis. This review analyses the need to shift to pyrolysis, mechanisms of pyrolysis, products and applications, pre-treatment processes, environmental effects, selection of zeolite or non-zeolite catalysts. Finally, the best suited mechanism, pre-treatment processes and reactors for various applications are enlisted.

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