Biomass Energy: A Review on Waste to Energy Approaches

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Abstract—Although Malaysia is blessed with significant reserves of fossil fuels, the crisis of these non-replenishable energy resources is foreseen with escalating human population. Fortunately, Malaysia is an agroindustry-based country while transforming into a manufacturing-based country. It is believed that the tremendous biomass waste sourced from various industrial sectors could be ameliorated into renewable biomass energy. Therefore, this paper reviews four major approaches that facilitate the conversion of biomass waste into energy, particularly gasification, fast pyrolysis and liquefaction, transesterification, and hydrolysis. It is worthwhile to declare that these pathways generate energy and mitigate environmental issue concurrently.

Keywords-Biomass; Waste; Energy

1. INTRODUCTION

The depletion of fossil fuel issue gained intensified attention as it is the prominent source of electrical energy for the past centuries. Recently, the biomass energy received great notability by virtue of its carbon-neutral characteristics, whereby photosynthetic species (plants or bacteria) will uptake the carbon dioxide produced from biomass energy extraction [1]. Biomass is an inexhaustible source of carbon as its organic constituents are originated from animal or plant, which can segregate into two major divisions namely virgin biomass and biomass waste [1]. The virgin biomass comprises of terrestrial biomass (grasses, trees, shrubs, cultivated crops, energy plants, and etc) and aquatic biomass (algae, seaweed, aquatic plants, and etc). Owing to the food scarcity in worldwide, the purpose of energy crops plantation for biomass waste as feedstock for biomass energy. Generally, there are four classic ways to transform biomass waste into energy, which inclusive of gasification, fast pyrolysis and liquefaction, transesterification, and hydrolysis. Remarkably, the end products of aforementioned pathways are different from each other, thereby renders different application in exploitation of biomass energy.

2. REVIEW ON GASIFICATION

Gasification can be defined as the thermochemical conversion of carbonaceous substances into combustible gaseous products primarily syngas, via oxidation with gasifying agents such as air, steam, oxygen, carbon dioxide, or their mixture at elevated temperature [2]. To date, the existing biomass gasification technologies that discovered include air gasification, steam reforming, dry reforming, partial oxidation, autothermal reforming, aqueous phase reforming, and solar reforming [3-8]. The classification of gasification technologies is accomplished in Table 1 together with their peculiar feature.

| e of gasification | Description | rmodynamic nature | erence |
|---------------------|--|---|--------|
| Air gasification | r as gasifying agent. | Exothermic $(\Delta H^o_{reaction} < 0)$ | [8] |
| Steam reforming | ₂ O as gasifying agent. | Endothermic $(\Delta H_{reaction}^o > 0)$ | 2, 4] |
| Dry reforming | O ₂ as gasifying agent. | Highly endothermic $(\Delta H_{reaction}^o > 0)$ | [2] |
| Partial oxidation | $_2$ as gasifying agent but the oxygen supplied is less retical amount of complete combustion. | Exothermic $(\Delta H^o_{reaction} < 0)$ | [7] |
| othermal reforming | system of steam or dry reforming with partial | ly thermodynamic neutral ($\Delta H^o_{reaction} ≈ 0$) | [3] |
| ous phase reforming | t a relatively low temperature $(200 - 240^{\circ}C)$ and essure $(30 - 50 \text{ bar})$. | Endothermic $(\Delta H_{reaction}^o > 0)$ | [4] |
| Solar reforming | olar energy for driving endothermic reforming | _ | [6] |

Table 1: Classification of gasification technologies

Essentially, syngas which is a mixture of H_2 and CO become attractive because it can serve as synthetic fuel for energy generation and feedstock for many downstream chemicals [9]. The syngas can be readily transformed into diverse valuable products, such as hydrogen via water gas shift reaction, ethanol via syngas fermentation, methanol via methanol synthesis, and alkanes via Fischer-Tropsch process [10]. Interestingly, the quantity and quality of the syngas produced will be influenced by gasifying agent employed in different gasification technologies, which engenders syngas with various proportions of CO, H_2 , CO₂, CH₄, and N₂[10].

Candidly, every gasification technology proposed has its respective superiority and drawback. Owing to the bountiful nitrogen content (78.09%) in the air as a diluent, air gasification eventually yields syngas with low heating value despite air can obtain at near-zero cost [1]. Partial oxidation process renders syngas with higher quality, nonetheless, the usage of pure oxygen as gasifying agent incurs a high operating cost [11]. Appealingly, steam reforming is well suited for liquid biomass to eliminate additional expenditure on external steam supply; concurrently, it generates a hydrogen-rich syngas due to the water gas shift side reaction, which is suitable for energy generation but not apt for methanol and Fischer-Tropsch synthesis [1, 9].

On the other hand, dry reforming process is acknowledged as the green reforming approach as it utilizes the greenhouse gas carbon dioxide as the oxidizing agent, nevertheless, its usage is discouraged by its highly endothermic nature which corresponds in a higher energy demand [12]. Comparatively, the syngas harvested from dry reforming typically exhibits a lower H₂:CO ratio, which may allude to the occurrence of H₂-consuming side reactions such as CO₂ methanation and reverse water gas shift [13]. Other than preheating of reactants, autothermal reforming nearly requires no external heat source because the endothermic steam or dry reforming will be sustained by the exothermic partial oxidation and preceding preheat [14]. However, this energy optimized autothermal reforming is counteracted by the fact that addition of oxygen ultimately discourages H₂ and CO production [15].

The newly touted aqueous phase reforming that executed at relatively low temperature is more energy efficient since it dispenses the need to vaporize water and organic compounds in biomass [4]. Moreover, aqueous phase reforming could be customized for waste treatment or simultaneous production of different chemicals in either gaseous or liquid state from a feedstock [4]. Coincidentally, aqueous phase reforming is performed at the favourable condition of water gas shift reaction, leading to the formation of hydrogen-rich syngas [10]. Its elevated pressure condition indicates the necessity of extensive monitoring on reactor though it is advantageous for subsequent H_2 purification from CO [16]. For the solar reforming, the endothermic steam or dry reforming reactor is heated using solar thermal energy instead of employing a conventional furnace, whereby the solar heat is applied to the reactor either directly or indirectly via a working fluid [17].

3. **REVIEW ON FAST PYROLYSIS & LIQUEFACTION**

Instead of extracting syngas from biomass feedstock via gasification, pyrolysis and liquefaction are two alternative promising routes that manufacture liquid synthetic fuel particularly bio-oils from biomass [10]. Bio-oils are defined as dark brown liquid with distinctive odor, whereby its composition varies accordingly to the feedstock (dirt, moisture content, and protein content), pyrolysis condition (heat transfer rate, temperature, and residence time), separation

condition (efficiency of condensation and char removal system), and storage (temperature, period, and air exposure) [10].

Typical bio-oils are comprised of acids, esters, alcohols, ketones, aldehydes, miscellaneous oxygenates, sugars, furans, phenols, guaiacols, and syringols [18]. It is speculated that the depolymerization and fragmentation of three major lignocellulose constituents available in biomass, *viz.* cellulose, hemicellulose, and lignin give rise to the multicomponent nature of bio-oils [10]. It is discovered that hemicellulose and cellulose fractions contribute to the formation of miscellaneous oxygenates, sugars, furans and phenols, whereby these compounds probably decompose to form acids, esters, alcohols, ketones, and aldehydes [10]. Meanwhile, the guaiacols and syringols are sourced from the lignin fraction [10].

For energy generation purpose, bio-oils are seldom directly employed as fuels attributed to its high water content, viscosity, ash content, oxygen content, and corrosiveness [19]. Hence, bio-oils are generally transformed to value-added fuels, such as syngas via steam reforming, hydrogen via steam reforming followed by water gas shift reaction, and upgraded bio-oils via hydrotreating, hydro-cracking, or emulsification [19]. Bio-oils not only bound to its utilization as synthetic fuel for heat and power generation; in fact, it is capable to serves as valuable chemical feedstock since more than 400 organic compounds were found within it [10]. Contemporary, bio-oils are used for the production of anhydrosugars, fertilizers, acids, agrochemicals, adhesives, liquid smoke, and wood flavor [19].

Pyrolysis is defined as thermal decomposition of carbonaceous materials in the absence of oxygen which yields carbon-rich char, bio-oils from condensable vapors, and syngas from non-condensable vapors [20]. As shown in Table 2, pyrolysis could be further classified into slow pyrolysis, intermediate pyrolysis, and fast pyrolysis based on the temperature, heating rate, residence time, and feedstock size adopted [21, 22]. For pyrolysis with long residence time, low temperature produces primarily char while syngas is the main product for high temperature [10].

| Туре | perature (°C) | Rate (°C/s) | nce time (s) | :k size (mm) | Product yield (%) | | | |
|-----------------|---------------|-------------|--------------|--------------|-------------------|-------|------|--|
| | | | | | -oil | -char | ngas | |
| v pyrolysis | 00 - 550 | .1 – 1 |) – 550 | - 50 | - 50 | - 35 | - 50 | |
| liate pyrolysis | 00 - 450 | 8 – 5 | 5 - 10 | < 1 | - 50 | -40 | - 30 | |
| pyrolysis | 00 - 1000 | -1000 | < 0.5 | < 0.2 | - 75 | - 25 | - 30 | |

Table 2: Typical pyrolysis parameters and product yields [21, 22]

Fast pyrolysis is capable to give high yield of bio-oils, but with three pre-requisite features, specifically fine particle size for high heat transfer rate, well monitored temperature in the range of $450 - 550^{\circ}$ C to minimize gasification, and a quenching system for condensation of pyrolysis vapors to prevent cracking [23]. Typically, fast pyrolysis-derived bio-oils are acidic liquor (pH around 2.5) that chemically unstable with time and temperature change, which possesses a higher oxygen content and moisture content that contribute to lower heating value relative to conventional fuel oil and liquefaction oil [10].

On the contrary, liquefaction is a thermochemical process whereby biomass feedstock is converted into bio-oils at elevated pressure (50 - 200 atm) and low temperature $(250 - 450^{\circ}\text{C})$ [10]. Liquefaction is more economical than pyrolysis for thermochemical conversion of wet biomass feedstock since it does not requires drying pre-treatment [24]. Principally, most liquefaction technologies discovered could be categorized into hydrothermal liquefaction, hydropyrolysis, or solvolysis according to the choice of solvent used [10]. Table 3 clearly portrays the dissimilarity between three types of liquefaction aforementioned.

| Table 3: Classification of liquefaction and its associated description [| 10] | |
|--|-----|--|
|--|-----|--|

| Type of liquefaction | Description | |
|---------------------------|---|--|
| Hydrothermal liquefaction | ater as a solvent. | |
| Hydropyrolysis | liquid solvent is required but involves high-pressure hydrogen and a heterogeneous | |
| Solvolysis | high-pressure liquefaction that employs a reactive liquid solvent such as creosote oil, col, simple alcohols, and phenol. | |

As compared to gasification and pyrolysis, liquefaction demands a lower energy input by virtue of its relatively low reaction temperature [24]. In addition, the introduction of a suitable solvent in liquefaction could dilute product concentrations, which ensuingly impedes undesired tar formation from cross-linked reactions between hydrocarbons and aromatic compounds [24]. Liquefaction is also able to reduce the oxygen content of products, hence renders the manufacture of bio-oils with lower moisture content and higher heating value [10, 24].

4. **REVIEW ON TRANSESTERIFICATION**

The urge for surrogate diesel fuel is amplified by the impending exhaustion of finite fossil fuels, therefore the biodiesel production via transesterification become an alluring process for the scientific community. Despite vegetable oils can be used directly in diesel engines, its direct usage is opposed by low volatility, high viscosity features, and problematic engine issues (such as oil ring sticking, carbon deposits, thickening of lubricating oils, and coking on the injectors) [10].

In transesterification or alcoholysis, the triglycerides present in biomass (particularly vegetable oil, animal fat, and microalgae oil) are converted into mono-alkyl esters (biodiesel) and glycerol upon the addition of excess monohydric alcohol (containing one hydroxyl group), typically in the presence of acid or base catalysts [10, 25]. The biodiesel produced from transesterification can either used directly or blended with petroleum diesel up to 20 vol%, in which the former requires slight modification on a diesel engine [10].

Transesterification comprises of three consecutive reversible reactions, *viz.* triglyceride reaction that forms mono-alkyl esters and diglycerides, diglyceride reaction that produces mono-alkyl esters and monoglycerides, and monoglyceride reaction that yields mono-alkyl esters and glycerols [10]. For improvement of biodiesel yield, there are two common strategies that can adopt to shift the reaction equilibrium towards product formation, such as continuous removal of mono-alkyl esters during reaction and employment of excess alcohol [10].

To date, there are diverse types of catalyst have been developed for transesterification of biomass into biodiesel, which includes homogeneous base or acid catalyst, heterogeneous base or acid catalyst, and biocatalyst lipase [26]. Verma, et al. [26] have thoroughly compared the pros and cons for each type of catalyst in transesterification, which is presented in Table 3. Typically, homogeneous catalyst able catalyze the transesterification faster than heterogeneous catalyst and biocatalyst lipase at the expense of difficult downstream processing for catalyst removal [10]. Meanwhile, heterogeneous catalyst not active as a homogeneous catalyst due to mass transfer limitation but it is easier for removal [10]. Biocatalyst lipase capable to produce by-products free biodiesel in spite of its high cost.

| ype of catalyst | Pros | Cons |
|-------------------|--|--|
| mogeneous base | the reaction rapid than homogeneous acid, | ks with oils with lower fatty acid content. |
| | us catalyst, and biocatalyst lipase. | e to undesired soap formation when free fatty acid |
| | ergy required to achieve equilibrium and mild | %. |
| | | great amount of wastewater due to the necessity of |
| | d abundant. | n step. |
| | | ld due to soap formation and wastewater. |
| mogeneous acid | the reaction rapid than heterogeneous catalyst and | ger time to achieve equilibrium. |
| | pase. | se corrosion on reactor and pipelines. |
| | th oils regardless of free fatty acid and water | separation of the catalyst from biodiesel. |
| | | |
| | itilize inferior quality raw material for biodiesel | |
| terogeneous base | the reaction rapid than heterogeneous acid and | tore away from air to prevent become poisonous. |
| | pase. | ks with oils with lower fatty acid content. |
| | easier separation of the catalyst as compared to the | e to undesired soap formation when free fatty acid |
| | is catalyst. | %. |
| | cheaper and more viable process credited to the | soap formation lowers product yield and renders |
| | f catalysts. | fication. |
| terogeneous acid | he reaction rapid than biocatalyst lipase. | ted catalyst synthesis procedures. |
| | ed for oils with higher fatty acid content. | tensive. |
| | tilize inferior quality raw material for biodiesel | ontamination may arise due to the leaching of |
| | | ve sites. |
| | the simultaneous occurrence of esterification and | emperature, higher alcohol to oil molar ratio and |
| | ation. | on time are generally needed. |
| | easier separation of the catalyst as compared to the | |
| | is catalyst. | |
| locatalyst lipase | ad to any by-products. | e enzyme. |
| | easiest separation of products. | ed easily due to feed impurities. |
| | tion conditions (low temperature). | onitoring is needed to prevent denaturation of the |
| | both esterification and transesterification of free | |
| | one step. | |

In addition, non-catalytic transesterification also has been touted as new promising technologies for biodiesel production, which is achievable via the employment of either co-solvent at atmospheric pressure and near ambient temperature or supercritical solvent at high pressure and temperature [27]. The introduction of co-solvent such as

tetrahydrofuran which is miscible with alcohol and oil could potentially overcome initial lag time of transesterification that caused by the low solubility of triglycerides in alcohol [10, 27]. Under the emerging supercritical technology, the alcohol solvent not only serves as the reactant but also as an acidic catalyst at high temperature and pressure [27].

Significantly, there are some advancements in biodiesel production via transesterification by integration with several physical technologies, namely microwave, ultrasonication, and membrane technology [28]. Instead of conventional heating, microwave-assisted transesterification incorporates the microwave irradiation that induces molecular attrition and collisions, which generates localized heating and subsequently accelerates the reaction, thereby gives high conversion with shorter time and reduced energy [28]. Ultrasonic-assisted transesterification utilizes ultrasonic irradiation that promotes effective emulsification of oil and alcohol, which greatly enhances the mass transfer between liquid-liquid boundary [28]. Membrane-assisted transesterification permits the continuous removal of biodiesel from reaction medium via a catalytic membrane, which resolves the equilibrium reaction limitation [28].

5. REVIEW ON HYDROLYSIS

Lignocellulosic biomass refers to plant biomass that composed of three constituent hydrolyzable biopolymers, *viz.* cellulose, hemicellulose, and lignin, whereby generally cellulose is the most abundant species [29]. Hydrolysis also grants energy extraction from biomass, in which the lignocellulosic biomass is broken down to their respective monomers units, particularly disintegration of biomass into cellulose, hemicellulose, and lignin; decomposition of cellulose into glucose; degradation of hemicellulose into its hydrolysates [10, 29].

Cellulose is a linear and water-insoluble biopolymer that composed of cellobiose units formed from the condensation of three D-glucose via β -1,4 glycosidic bonds [29]. Partial acid hydrolysis of cellulose yields intermediate products such as cellotetraose (glucose tetramer), cellotriose (glucose trimer), and cellobiose (glucose dimer) while complete acid hydrolysis gives fermentable product glucose [10]. Enzymatic hydrolysis of cellulose by cellulase also permits glucose production with the necessity of a pre-treatment because limited cellulase accessibility to cellulose due to high crystallinity of cellulose, extensive intermolecular hydrogen bonding and van der Waals forces, and obstruction by hemicellulose and lignin [10, 29].

Hemicellulose is a branched heteropolysaccharide chiefly composed of pentose (five-carbon monosaccharides such as xylose, arabinose) and hexose (six carbon monosaccharides such as mannose, glucose, galactose, and rhamnose) sugar monomers, which serves as the linkage between cellulose and lignin [29, 30]. Hemicellulose exhibits amorphous nature due to its branched structure, thus it is easier to hydrolyze into its monomer sugars as compared to cellulose with high crystallinity and degree of polymerization [29]. Meanwhile, lignin is a highly branched, non-carbohydrate, and mononuclear aromatic biopolymer, which provides the plant mechanical support and resistance against microbial or enzymatic degradation owing to its complex and cross-linked aromatic structure [10, 29, 30].

The aqueous phase sugars (hexose and pentose) sourced from hydrolysis of cellulose and hemicellulose fractions, can be readily converted into various gaseous and liquid fuels either via a chemical or biological pathway. To date, the technologies that facilitate the conversion of aqueous phase sugars into biofuels include bioalcohol production via fermentation, methane production via anaerobic fermentation, hydrogen production via dark fermentation, alkane synthesis via aqueous phase reforming, and syngas generation via various reforming [10, 29]. On the other hand, the most recalcitrant by-product lignin can be transformed into biogasoline via a stepwise depolymerization-hydroprocessing (hydrogenation, hydrocracking, and hydrotreating) system [10].

Table 4 summarizes the various type of proposed pre-treatments for hydrolysis, together with their pros and cons [10, 29, 31]. Ultimately, all pre-treatments alter the structure of biomass to ease downstream processing by several strategies, such as reduce the crystallinity of cellulose, increase biomass surface area, remove hemicellulose, and break lignin seal [10]. As shown in Table 4, pre-treatment methods for hydrolysis could be classified into physical, chemical, biological, or physicochemical process based on the nature of the process mechanism.

Basically, there are three types of hydrolysis used for the generation of aqueous phase sugars and lignin, namely enzymatic hydrolysis, acid hydrolysis, and supercritical hydrolysis [29]. Enzymatic hydrolysis of lignocellulosic biomass by cellulase is feasible after pre-treatment, whereby the cellulase activity is influenced by substrate concentration, end-product inhibition, reaction temperature and pH [29]. Cellulase is a mixture of endoglucanase, exoglucanase, and β -glucosidase that catalyzes hydrolysis of cellulose to glucose, specifically endoglucanase cleaves β -1,4 glycosidic bonds in the long chain to create free chain ends; exoglucanase acts on free chain ends progressively to liberate oligosaccharides; β -glucosidase converts these oligosaccharides into glucose [10, 29].

Moreover, the lignocellulosic biomass can also be hydrolyzed into glucose via acid hydrolysis, which either employs concentrated acid or dilute acid for cleavage of the glycosidic bonds via a different mechanism [29]. For concentrated acid hydrolysis that operates at low temperature $(20 - 50^{\circ}C)$ and atmospheric pressure, the concentrated acid can enter the cellulose via osmosis, which renders swelling of cellulose and thereby leads to breakage of glycosidic bonds [29]. Although concentrated acid hydrolysis has low energy requirement, it raises problematic issues regards equipment corrosion and acid recovery [29].

For dilute acid hydrolysis that typically operates at temperatures > 180° C and pressures of 1.2 - 1.3 MPa, the hydrated protons protonate the oxygen in glycosidic bonds which eventually results in its cleavage [29]. The reaction condition of dilute acid hydrolysis give high cellulose conversion but low selectivity of glucose [29]. A newly introduced supercritical hydrolysis allows the hydrolysis of lignocellulosic biomass in water without catalyst needed, with the pre-requisite of high temperature and elevated pressure [29]. It is believed that high temperature used in supercritical hydrolysis enhances the ionization of water into hydrogen ion and hydroxyl ion, hence the water become a weakly-polar solvent that can dissolve lignocellulosic biomass for its hydrolysis [29].

| Туре | Pre-treatment | Pros | Cons |
|-----------------|---|--|---|
| Physical | Chipping, grinding, milling, comminution, and thermal methods | • Effective for reducing particle size and crystallinity of biomass. | • More energy intensive as compared to chemical pre-treatment. |
| Biological | Lignin degradation | Mild condition (low temperature).Low cost. | Low rate of hydrolysis.Longer pre-treatment time. |
| Chemical | Acid | Increase the porosity of the substrate and accessibility of cellulose for cellulase. Able to solubilize hemicellulose. High glucose yield. | Equipment corrosion. Issues in the recovery and recycling of the acid. Formation of inhibitors. |
| Chemical | Alkaline | Can remove all lignin and part of hemicellulose.Low inhibitor formation. | Neutralization step is needed to remove lignin and inhibitors. Alteration of lignin structure. |
| Chemical | Ionic solvent | Able to hydrolyze lignin and hemicellulose. Capable to dissolve high loadings of different biomass. Mild condition (low temperature). | Need for solvent recovery and recycle. |
| Chemical | Wet oxidation | Able to solubilize hemicellulose and remove lignin. | Drying and milling usually needed before wet oxidation.Formation of inhibitors. |
| Physicochemical | Steam explosion | Cost effective.Able to transform lignin and solubilize hemicellulose.Give high yield of glucose and hemicellulose via a two-step process. | Only partially degrade hemicellulose. Require acid catalyst to make the process efficient for biomass with high lignin content. Generate toxic compounds. |
| Physicochemical | Liquid hot water | Fully separate hemicellulose from biomass.Do not require a catalyst.Able to hydrolyze hemicellulose. | High energy and water input. Need to handle the solid mass leftover (cellulose and lignin). |
| Physicochemical | Ammonia fiber explosion | Highly effective for herbaceous and low lignin content biomass. Increase the accessibility of cellulose. Cause inactivity between lignin and enzyme. Low inhibitor formation. | Need to recycle the ammonia. Less effective for biomass of high lignin content. Alter the structure of lignin. |
| Physicochemical | Ammonia recycle percolation | Able to remove most lignin content.Give high cellulose content.Most effective for herbaceous biomass. | High energy costs and liquid loading. |
| Physicochemical | Supercritical fluid | Give low degradation of sugars.Cost effective.Increase cellulose accessible area. | Require high pressure.Do not hydrolyze lignin and hemicellulose. |

 Table 4: Pros and cons of pre-treatment methods for hydrolysis of lignocellulosic biomass [10, 29, 31]

5. CONCLUSION

Conclusively, there are four major routes that transform biomass wastes into synthetic fuels, *viz.* gasification for syngas formation, fast pyrolysis and liquefaction for bio-oils manufacture, transesterification for biodiesel production, and hydrolysis for aqueous phase sugars or lignin synthesis that can serve as feedstock for fermentation or reforming. To reduce the overdependence of fossil fuel energy, it is envisaged that the vast quantities of biomass waste from various industrial sectors could be ameliorated into biomass energy via the discussed pathways. For the future perspective, it is foreseen that the aforementioned pathways not only offer a valorization approach but it also helps to overcome the scarcity problem of available landfills.

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