Thermochemical Approaches to Produce Bio-Oils for Epoxy Resins

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Contributor: Philip Agbo , Abhijeet Mali , Dongyang Deng , Lifeng Zhang

Bio-oils are produced from biomass using three main processing techniques, namely (i) organic solvent liquefaction, which involves the utilization of organic solvents at relatively low temperatures to liquefy biomass; (ii) fast pyrolysis, which involves the liquefaction of biomass at elevated temperatures in the absence of oxygen and a solvent; and (iii) hydrothermal liquefaction, which breaks down biomass in water at elevated pressures and temperatures. It is noteworthy that even though the products from the abovementioned three liquefaction processes are all called bio-oil, the properties of these bio-oils, such as hydroxyl number, chemical composition, and molecular weight, differ greatly. Therefore, the final physical properties of bio-oil-based epoxy resins depend on the processing conditions used for the corresponding bio-oils.

bio-oil epoxy resin thermochemical processing sustainable material

1. Introduction

Epoxy resins are a class of thermosetting pre-polymers and possess excellent physical properties, such as good processability, excellent mechanical strength, great chemical resistance, high adhesion strength, high thermal stability, and outstanding insulation capability after curing [1][2][3][4]. Epoxy resins are extensively used in a wide range of commercial products, including coatings, adhesives, and composite materials, for applications in industries such as transportation, construction, aerospace, electronics, etc.

Epoxy resins are generally derived from fossil fuels and produced through a series of chemical reactions. Diglycidyl ether of bisphenol A (DGEBA) is the most commonly used epoxy resin on the market, constituting about 75% of the overall epoxy resins [5]. DGEBA is produced by a condensation reaction between bisphenol A (BPA) and epichlorohydrin with a catalyst such as sodium hydroxide, as shown in **Figure 1**.

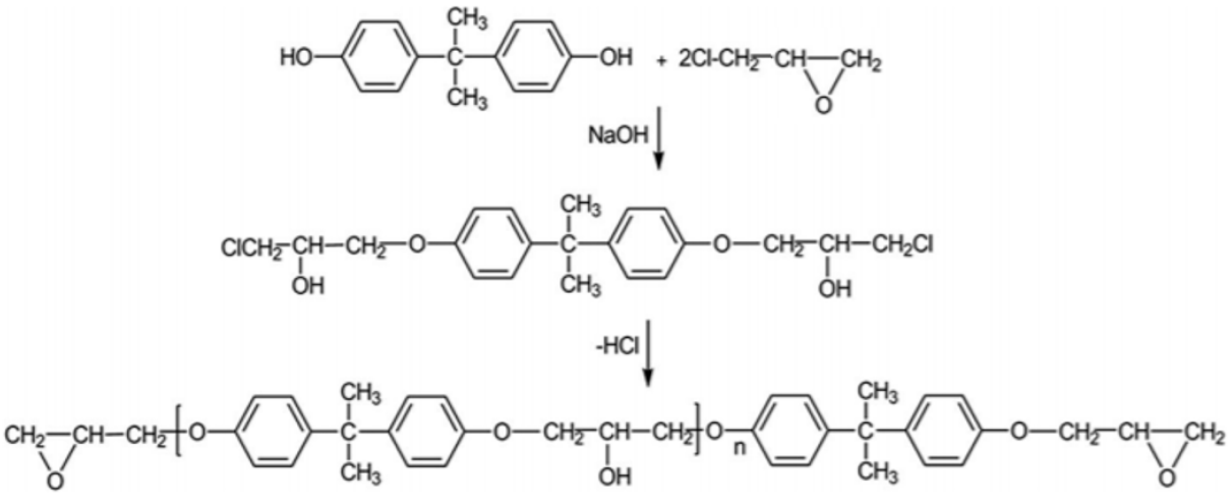


Figure 1. Synthesis of diglycidyl ether of bisphenol A (DGEBA) [6][7][8].

Epoxy resin must go through curing to solidify and achieve its final mechanical properties. In the curing process, a chemical compound (termed as curing agent or hardener) with two or more functional groups (e.g., amine functional groups, $-NH_2$) that can react with epoxide functional groups (a cyclic ether with a three-membered ring, also called oxirane) is added and reacts with epoxy resin, resulting in a crosslinked molecular network. The curing process can be accomplished through heat or light, e.g., heat curing or UV curing, and the final cured product is a thermoset polymer, which is stable and does not melt or dissolve.

2. Bio-Based Epoxy Resins

In recent years, bio-based epoxy resins have gained increasing attention due to the inception of sustainable development and expansion of the bioeconomy [9]. The environmental and economic concerns about petroleum-based epoxy resins as well as the unpredictability of limited petroleum resources have spurred considerable interest in the research and development of epoxy resins that are synthesized or modified with bio-oils via thermochemical processing along with the epoxy resins from other natural/renewable resources such as vegetable oils, lignin, and sugars [10][11][12].

3. Organic Solvent Liquefaction

Organic solvent liquefaction is a thermochemical liquefaction process that makes use of functional groups from organic solvents and biomass to convert biomass into bio-oil. The generated bio-oil products can be utilized as precursor materials to synthesize epoxy resins as well as other polymers [13]. Organic solvent liquefaction usually takes place under high pressure in a relatively low-temperature ambience (<250 °C). In the course of organic solvent liquefaction process, biomass initially breaks down to smaller, reactive, and unstable molecules in appropriate solvent systems and undergoes re-polymerization and/or re-condensation to form a variety of bio-oil molecules with a various range of molecular weights [14][15][16][17]. Suitable solvents are selected to help reduce undesired reactions that lead to solid products and thus promote liquid-state bio-oil formation [16]. Different solvents

can result in different liquefaction efficiencies, and a higher liquefaction yield has been observed with solvents that have a higher dielectric constant [18]. Some common solvents used in organic solvent liquefaction include dioxane, ethylene glycol, polyethylene glycol, ethylene carbonate, phenol, etc. [13][16]. One significant advantage of organic solvent liquefaction is that the feedstock does not need to be dried to proceed [16], while one big challenge in producing bio-oil via organic solvent liquefaction is that this processing technique requires more sophisticated and costly reactors [15].

4. Fast Pyrolysis

Fast pyrolysis (also called flash pyrolysis) is another biomass liquefaction process that takes place at elevated temperatures (400–600 °C) in the absence of oxygen and a solvent, in which fast cooling of vapors and aerosols in the processing generates bio-oil for the synthesis of epoxy resins. As a liquefaction process, fast pyrolysis can produce bio-oil with a yield as high as 70–80% depending on processing conditions such as temperature, residence time, etc. [19]. A typical fast pyrolysis system comprises a series of operations, beginning with a biomass feedstock such as wood, rice husk, or others (**Figure 2**) [20]. The essential conditions needed to obtain a high yield of bio-oil through fast pyrolysis include a fine particle size (<1 mm), moderately high pyrolysis temperature (450–500 °C), very high heating rate (>200 °C/s), short vapor residence time (<4 s), and rapid cooling of pyrolysis vapors.

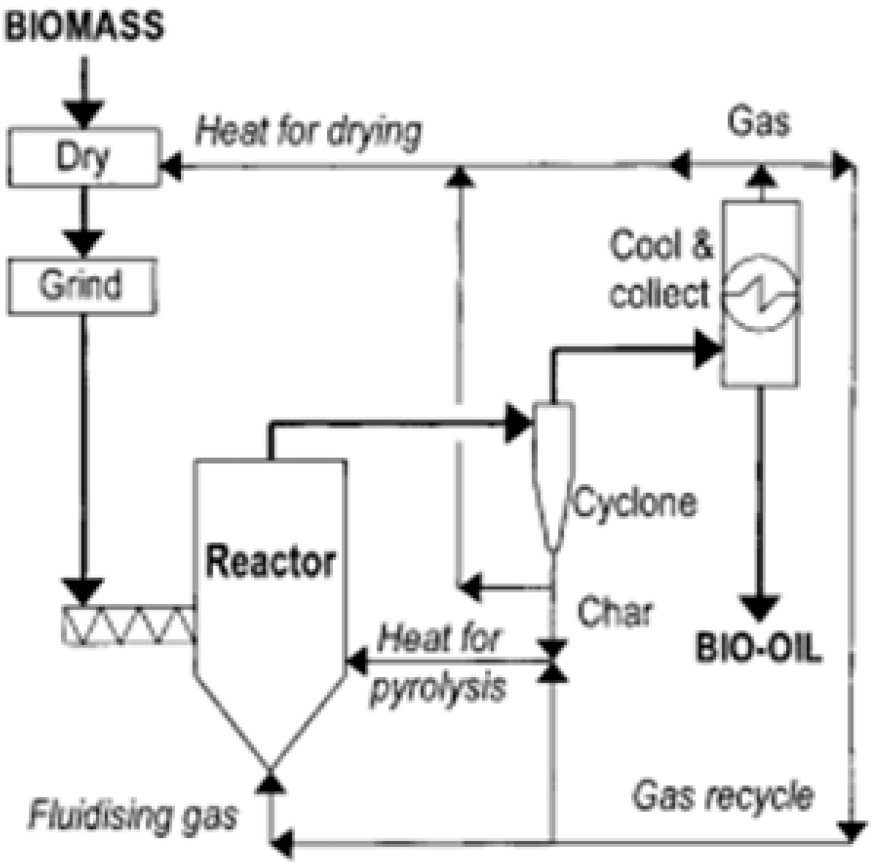
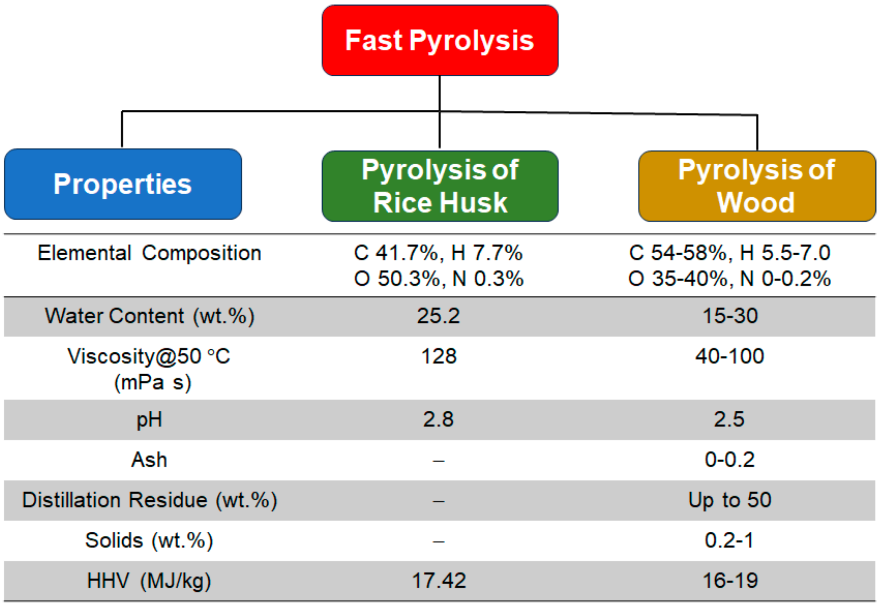


Figure 2. Schematic diagram of fast pyrolysis system [20].

The bio-oil produced from the fast pyrolysis of lignocellulosic biomass is usually a free-flowing liquid that is dark brown in color with a hydrophilic phase and a hydrophobic phase [19][21][22]. The hydrophobic phase is rich in pyrolytic lignin and so has the potential to supplant bisphenol A to produce bio-oil-based epoxy resins. The yield and quality of bio-oil produced from fast pyrolysis depend on both the processing parameters and specific biomass being employed (**Figure 3**) [23]. For example, the bio-oil produced from pyrolysis of rice husk exhibited excess water content and a higher level of viscosity than the one produced from pyrolysis of wood.



Properties	Pyrolysis of Rice Husk	Pyrolysis of Wood
Elemental Composition	C 41.7%, H 7.7% O 50.3%, N 0.3%	C 54-58%, H 5.5-7.0 O 35-40%, N 0-0.2%
Water Content (wt.%)	25.2	15-30
Viscosity@50 °C (mPa s)	128	40-100
pH	2.8	2.5
Ash	–	0-0.2
Distillation Residue (wt.%)	–	Up to 50
Solids (wt.%)	–	0.2-1
HHV (MJ/kg)	17.42	16-19

Figure 3. A comparison between bio-oils from fast pyrolysis of rice husk and wood in terms of properties [23].

5. Hydrothermal Liquefaction

Among the three biomass liquefaction processes, hydrothermal liquefaction is a favorable technique to synthesize bio-oil with a significant potency for commercial use due to having the most affordable cost [24]. The biomass that has been used in research so far as feedstock for hydrothermal liquefaction has had high lignin and cellulose contents. The research results over recent years, as shown in **Table 1**, indicate that hydrothermal liquefaction is a practicable technique for the transformation of biomass to bio-oil [25]. Unlike organic solvent liquefaction, hydrothermal liquefaction uses water as the liquefying solvent at sub- or super-critical conditions to convert lignocellulosic biomass into bio-oil [5]. Depending on the hydrothermal parameters that are employed in the processing, the hydrothermal liquefaction of lignocellulosic biomass can provide a bio-oil yield in the range of about 30–40 wt.% [26]. Moreover, the yield of hydrothermally liquified bio-oil can be increased to about 65 wt.% when ethanol is used as a co-liquefying solvent along with water [27]. Furthermore, Celikbag et al. [28] examined the effects of ethanol and temperature on the number of hydroxyl and carbonyl groups in a bio-oil product produced from hydrothermal liquefaction of loblolly pine. The results indicated that addition of ethanol as a co-solvent increased overall hydroxyl number of the generated bio-oil but decreased the number of phenolic-type hydroxyl groups in the bio-oil.

Table 1. Hydrothermal liquefaction of various biomasses to produce bio-oils as discussed in the literature.

Feedstock	Temperature (°C)	Pressure (MPa)	Time (s)	Yield of Oil (%)	Calorific Value (MJ/Kg)	Reference
Dairy Manure	250–380	10–34	–	50	–	[29]
Sewage Sludge	300	10	30–1200	48	37–39	[30]
Rubbish	250–340	6–8	360–7200	27.6	36	[31]
Sewage Sludge	150–300	8–20	0–10,800	44.5	35.7	[32]
Sewage Sludge	250–350	8–20	–	30.7	36.4	[25]
Municipal Solid Waste	260–340	13–24	–	32	46	[33]
Municipal Solid Waste	295–450	–	1200–5400	35–63.3	–	[34]
Sewage Sludge	300–360	10–18	5–20	–	30–35	[35]
Swine Manure	305	10.3	80	70	25–33	[36]

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