ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 5, pp. 1006–1012. © Pleiades Publishing, Ltd., 2012.
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Thermal Methods to Obtain Liquid Fuels and Other Products from Wood

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Received November 1, 2010

Abstract—The present state and prospective directions of wood thermochemical liquefaction are considered and summarized, including hydrothermal liquefaction, liquefaction in organic solvents, and major methods of pyrolysis. The most promising techniques among them are liquefaction in formic acid and phenols and fast pyrolysis methods.

DOI: 10.1134/S1070363212050350

Plant biomass and, in the first place, wood hold a special place among other renewable energy sources, such as energy generated by hydropower plants, wind energy, geothermal energy etc., which do not allow obtaining liquid fuels directly. In this respect plant raw materials possess a significant advantage, i.e. they can be chemically processed into motor or boiler fuels. Therefore, the problem of energy use of wood and, in a broader sense, of plant materials (including agricultural waste) takes on special importance. Production of liquid fuels from wood is also environmentally sound, as it does not disrupt the balance of carbon dioxide production and consumption in the atmosphere and, therefore, has no influence on the greenhouse effect.

Development of legislative acts regulating carbon dioxide emissions into the atmosphere, increasing costs of petroleum products, and the necessity of rational use of plant resources encourage the development of energy use of wood as a renewable source for production of liquid fuels.

Negative consequences of biofuel production using plant raw materials include reductions in cultivated areas.

Dry wood contains 49–50% of carbon, 43–44% of oxygen, and ~6% of hydrogen. The main components of wood are cellulose, hemicelluloses (~70%), and lignin (up to 30%). The specific feature of wood is its low ash content, below 1% [1]. Besides, wood and fuels obtained from wood contain no sulfur-containing compounds.

Due to high oxygen content in wood and other types of plant raw materials the obtained fuels have lower calorific capacity that liquid hydrocarbon fuels (Table 1).

Special attention should be paid to names of fuels given in Table 1. At present there is no common terminology with regard to liquid products of thermal conversion of plant materials. They are called pyrogenous tars, bio-petroleum, bio oils, or simply oils. In this work we will stick to the names used by the authors of the cited work. Names of liquid intermediate and marketable products applied in the Russian wood chemical industry can be found in monograph [2].

There are several ways to use wood as an energy source: direct combustion, gasification, pyrolysis, and liquefaction of wood by fermentation or thermal treatment.

Usually when assessing the efficiency of a particular method of using wood as a fuel source major attention is paid to completeness of biomass conversion. In our opinion, one of the main criteria for the assessment should be the degree of transformation of the biomass potential energy into the end product heating value, i.e. energy efficiency of the process. It should be noted that often energy expenses of the conversion process are not taken into account, although such costs can be significant, especially for processes based on fermentation. All this also completely applies to costs related to biomass transportation and

Table 1. Energy characteristics of wood and liquid fuels obtained from wood

Fuel type	Density, kg m^{-3}	Heating walue (lower), MJ kg^{-1}	Energy density, GJ m^{-3}
Wood shavings	90	18.0	1.6
Sawdust	130	18.0	2.3
Wood chips	400	18.0	7.2
Pellets	650	18.0	11.7
Charcoal	300	30.0	9.0
Charcoal briquettes	650	30.0	19.5
Methanol	796	22.2	17.7
Ethanol	800	28.0	22.4
Butanol-1	803	33.1	29.2
Diesel fuel	800	45.0	36.0
Heavy fuel oil	960	40.0	38.4
Ensyn bio oils (Canada)	1180	23.1	27.3
Dynamotive bio-petroleum (Canada)	1200	23.0	27.6
Settled pyrogenous tar	1086	29.5	32.0
Soluble pyrogenous tar	1180	28.6	33.7
Total pyrogenous tar	1150	29.0	33.3

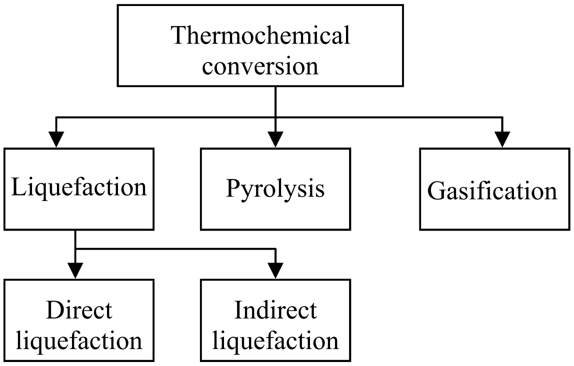
preparation, including shredding. Consideration of these costs can change the perception about profitability of one or another method to use plant raw materials for energy purposes. Unfortunately, there are no comprehensive studies demonstrating comparative effectiveness of various methods of wood processing for energy purposes. We can only note that according to monograph [3] the most economically attractive technique is biomass pyrolysis, which makes it possible to produce liquid fuels.

Various methods of thermochemical conversion of biomass are used in order to obtain fuels and other valuable products from plant raw materials (see the figure) [4, 5–13].

The processes of wood liquefaction through fermentation or thermal liquefaction has the following advantage: they make it possible to obtain liquid fuels, which are easy to store and apply in vehicles. Obtainment of alcohols and, first of all, fuel ethanol from the carbohydrate component of wood or other plant raw materials is a well-known process requiring no complicated equipment.

Liquefaction methods require no preliminary separation of wood into components, i.e. cellulose and lignin. One of the exceptions is the liquefaction of so called hydrolysis lignin. A significant advantage of the thermal liquefaction method as compared to gasification and pyrolysis of wood is that there is no need for preliminary drying of wood. Moreover, it is also important that products of liquefaction could be used not only as fuels but also as source materials for obtainment of technically valuable products.

Fast pyrolysis of preliminary shredded wood is undoubtedly of interest. This process can be implemented in a continuous mode. Applicability of liquid fuels obtained through wood pyrolysis is limited by aromatic compounds formed during thermal deploymerization of lignin, which pass into liquid products of the pyrolysis. In a number of cases an additional



Methods of thermochemical conversion of biomass.

dearomatization stage is necessary for motor fuel production technologies.

According to European rules and standards for liquid pyrolisates [14], in order to evaluate the quality of fuels (Dynamotive, Ensyn etc.) the following five indicators are applied: homogeneity, water content, solids content, stability, and flash point. The influence of raw materials (soft and hard wood, wood with bark, and bagasse) on the pyrolisates' composition and physical properties is described.

This article gives an outlook to works dedicated to obtainment of fuels and other products through thermal liquefaction and pyrolysis of wood performed during the last decade. (The process of liquefaction in ionic liquids developed for obtainment of a number of valuable chemical products is not considered in this article).

Hydrothermal Liquefaction

Hydrothermal liquefaction of plant raw materials is carried out in an aqueous medium and requires no preliminary drying of the raw materials. Under conditions of hydrothermal liquefaction (in the best version to date) at 300–350°C biomass, e.g. wood chips, is converted to gaseous and liquid products (oils) with the yield of 30 and 50%, respectively, within a period of 5–15 min [4]. The content of phenols in the oils exceeds 50%. Unlike liquid products of pyrolysis, oils obtained as a result of hydrothermal liquefaction contain much less carbohydrates and organic acids.

Water acts as a chemical agent causing deploymerization of both the carbohydrate component of wood and lignin. Degradation products are highly soluble in hot water, which prevents their condensation and the formation of secondary solid products [15]. The use of water is in compliance with the green chemistry requirements and is not hazardous to the environment.

Water in supercritical state can dissolve substances that are not soluble in normal water and can ensure much higher concentrations of chemical agents, which decreases the influence of mass transfer on the reaction rate. The unique properties of water in supercritical state that are of interest for energy-chemical use of wood are described in work [15].

Efficiency of the hydrothermal liquefaction process can be increased through introduction of catalysts – hydroxides or carbonates of alkaline metals – into the reaction system. Hydroxides and carbonates of alkaline metals catalyze hydrolytic decomposition of cellulose and hemicelluloses, suppress the formation of carbonized residue, increase the yield of liquid products, and have a significant impact on the chemical composition of liquid products [16].

Thus, in a case of wood liquefaction in water (280–360°C, reaction time of 10–30 min) the maximum yield of organic substances extractable with acetone amounted to 24% [17], while in the presence of K_2CO_3 the yield of oils increased up to 30% [18]. As a result of cherry laurel wood liquefaction in water in the presence of NaOH and Na_2CO_3 (250°C and 350°C) the yield of liquid oils reached 69%, their calorific capacity amounting to 17.89 MJ kg^{-1} [19]. The maximum yield of oils (53%) from birch wood was achieved as a result of liquefaction in the presence of Na_2CO_3 at 380°C [20]. In case of poplar wood liquefaction in aqueous solutions of Na_2CO_3, K_2CO_3, and HCOOH the yield of oils reached 35% [21]. Treatment of pine wood with an aqueous solution of K_2CO_3 (250°C) ensured that within 15 min 8.5% of the wood was transformed into the following products: liquid products extractable with organic solvents, substances remaining in water after the extraction (7.5%), and gaseous products (45%) [22]. Pine wood liquefaction in water for 30 min at 300°C with the use of $Ca(OH)_2$ as a catalyst resulted in obtainment of 45% of heavy oils and 20% of water-soluble products, the calorific capacity of which amounted to 32 and 18 MJ kg^{-1}, respectively [23].

In order to study the mechanism of formation of products obtained as a result of hydrothermal liquefaction of the carbohydrate component of wood the model monosaccharides were used. It was determined in work [24] that treatment (340°C, 27.5 MPa, and 25–204 s) of diluted aqueous solutions of glucose and some other monosaccharides with acids caused mainly dehydration reactions with the formation of 5-hydroxy-methylfurfural, while catalysis with bases resulted in the formation of glycol and glycerol aldehydes. Further fragmentation and dehydration resulted in the formation of a number of low-molecular substances such as formic, acetic, and acrylic acids, as well as furfural and 1,2,4-trihydroxybenzene.

The authors of work [24] assume that products of hydrothermal processing of biomass can contain significant quantities of reactive aldehydes, which has a negative impact on the stability of obtained bio oils. Therefore, in order to produce more stable fuels subsequent deoxygenation of bio oils could be required. Investigations of glucose conversion into oils when heated to 300°C in water within a holding time of 30 and 60 min demonstrated that addition of HCOOH and $KHCO_3$ increased the conversion rate [25].

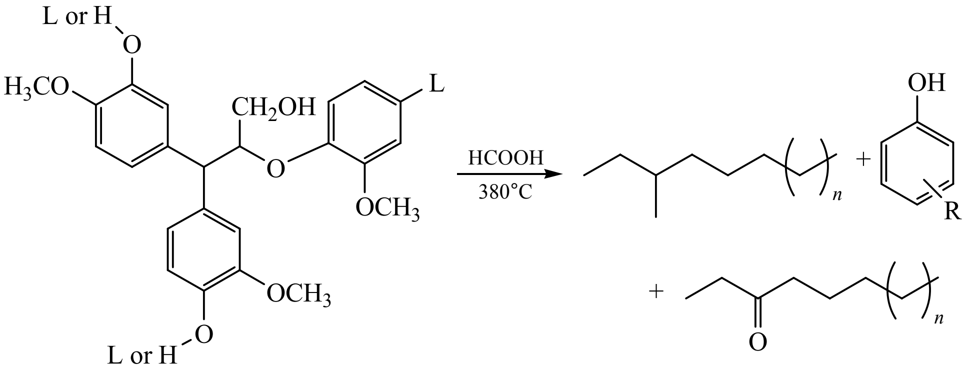
According to work [26], in the process of thermal degradation of organosolvent lignin in water in supercritical state with and without additions additions of phenol the latter interacted with intermediate products of degradation, thus suppressing secondary condensation, which contributed to the formation of low-molecular products. The degradation products included derivatives of guaiacol, catechol, and syringol.

Liquefaction in Organic Solvents

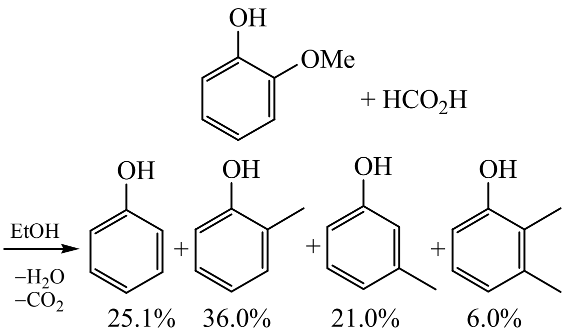
The process of wood liquefaction is most frequently carried out in a medium of formic acid and aliphatic alcohols, which act as hydrogen donors. It was demonstrated that depolymerization and deoxygenation of lignin were successfully performed using a mixture of formic acid and isopropyl alcohol [27].

The use of formic acid as a solvent made it possible to convert up to 95% of organosolvent lignin into soluble state at 380°C applying no catalysts [28–31]. The process is carried out in one stage, which is an advantage distinguishing it from the three-stage process of catalytic liquefaction proposed in patent [32]. The process results in the formation of easily separated aqueous and organic liquid phases, the latter consisting mainly of low-molecular alkylphenols. It is important that there are no polyaromatic hydrocarbons in the thermal conversion products. The calorific capacity of the obtained oils is estimated at 35–44 MJ kg^{-1}. The mechanism of formation of aliphatic hydrocarbons and alkylphenols with long-chain substituents remains unclear.

The scheme of lignin degradation resulting from heating in formic acid is given below on the basis of the achieved results [29]:



Experiments with guaiacol, a compound modeling the structural unit of lignin, demonstrated that deoxygenation of guaiacol (280°C, high pressure, 14 h) with the formation of methylphenols took place as follows:



In work [33] studying the process of cellulose liquefaction in phenol medium in the presence of H_2SO_4 (9.8% of the acid calculated to cellulose) it was found that the degree of conversion was determined by phenol/cellulose ratio, which should reach at least six. When the ratio is below four, condensation of the obtained products takes place with phenol acting as a chemical agent bonding individual fragments. The presence of catalytic quantities of acid is not necessary for solvolysis of wood with phenol. Thus, when birch wood flour is heated to 250–450°C in the absence of sulfuric acid, more than 30% of the initial wood is converted into soluble state [34].

In work [35] liquefaction of tallow tree wood in phenol at temperatures of 150–180°C and at various phenol/biomass ratios was studied. It was demonstrated that at first wood lignin decomposition took part; however, in case of phenol deficiency reactions of condensation of lignin degradation products started to proceed.

Liquefaction of polysaccharides in the presence of alcohols or phenol takes place through solvolysis of the glycosidic bond with the formation of the corresponding glycosides and their subsequent transformation into ethers of levulinic acid [36–38]. Investigations of solvolysis of poplar wood taken in the form of wood shavings with alcohols (*n*-octanol, ethylene glycol, and glycerol) demonstrated that the process consisted of several stages and included biomass dehydration and alcoholysis [38].

It was suggested that the key stage of lignin alcoholysis catalyzed by acids was the cleavage of β-alkyl-aryl ether bond [38, 39]. During investigations of the mechanism of lignin liquefaction in the presence of phenol and catalytic quantities of sulfuric, phosphoric, and oxalic acids, using a model compound of guaiacyl glycerol-β-guaiacyl ether as an example [40, 41], it was found that the key product of the reaction was guaiacyl glycerol-α-phenyl-β-guaiacyl ether. Based on the structure and yield of the reaction products it was suggested that the initial stage of the reaction involved condensation of phenol with ether (model compound) at the α-carbon atom, followed by cleavages of β-O-4 and C_β–C_γ bonds.

Attention of researchers is attracted to the processes of wood and lignin liquefaction in solvents in supercritical state, mainly in alcohol medium [42, 43]. Pine wood liquefaction in methanol at temperatures close to critical [44] results in the formation of products that can be used both for obtainment of fuels and as source materials for organic synthesis [45]. There is an opinion that the most promising results can be achieved in case ethanol is used. Thermal liquefaction of pine wood shavings was performed; the process was carried out in ethanol in the atmosphere of hydrogen at temperatures of 200–350°C in the presence of FeS and $FeSO_4$ as catalysts [46]. Under such conditions it was possible to convert up to 63% of wood into oils consisting mostly of phenols (calorific capacity of the oils reaching 29 MJ kg^{-1}). The process of wood liquefaction in aqueous-alcohol mixtures is more efficient than in pure alcohol. Solvolysis of wood in 50% aqueous alcohol (ethanol or methanol) at 300°C for 15 min results in the formation of bio oils with the yield of 65% [47].

Pyrogenous oils with the lower content of oxygen can be obtained by thermal degradation of wood in the atmosphere of hydrogen or carbon monoxide (or their mixture), as well as in a medium of hydrogen-donor solvents. As demonstrated by the study on liquefaction of wood shavings, the use of hydrogen-donor solvents drastically increases the efficiency of hydrogenolysis of wood shavings [48, 49]. The yield of oils reaches 67% and strongly depends on the temperature within a range of 200–350°C. For reductive depolymerization of lignin 9,10-dihydroanthracene (AnH_2) and its derivatives were used (AnH_2 being a stronger hydrogen donor than tetralin) [50]. The process requires large quantities of the solvent. The major disadvantage of such processes is the necessity of the solvent recovery.

In the processes of liquefaction with the use of catalysts side reactions can take place. Such reactions result in the formation of carbonaceous residue, thus reducing the catalyst activity. During investigations of the process of poplar wood liquefaction in glycerol within a temperature range of 170–290°C with additions of 5% of Na_2CO_3 and NaOH, as well as without addi-tions, it was determined [51] that 80–100% of the initial biomass could be converted into solution. Degradation products are characterized by a high calorific capacity. Application of glycerol reduces the surface tension of the solution at high temperatures, which contributes to better penetration of alkaline substances into wood and facilitates decomposition of wood.

Hydrogenolysis of organosolvent lignin in the presence of $Ru(Cl)_2(PPh_3)_3$ made it possible to convert more than 96% of lignin into soluble state [52]. It was demonstrated that during hydrogenolysis of lignin cleavages of aryl-O-aryl and aryl-O-alkyl ether bonds took place. Application of HZSM-5 zeolite catalyst makes it possible to convert up to 43% of organosolvent lignin into liquid products, consisting mainly of aromatic hydrocarbons [52].

Pyrolysis of Wood

There are several methods of wood pyrolysis that can be applied depending on whether the objective is to obtain solid, liquid, or gaseous products (Table 2).

The quantitative ratio of products formed as a result of pyrolysis of lignocellulosic material depends on the process conditions. The most effective way with regard to liquid products and their heating value is fast pyrolysis characterized by the following ratio: 50% of liquid products, 18% of charcoal, 20% of pyrogas, and 12% of water. In case of slow pyrolysis the ratio is as follows: 21% of liquid products, 35% of charcoal, 20% of pyrogas, and 24% of water.

In order to perform fast pyrolysis the following conditions should be observed [12]: extremely high

Table 2. Yield of products (in terms of dry wood) for different methods of pyrolysis [11]

Process	Conditions of pyrolysis	Liquid products, %	Charcoal , %	Gases, %
Fast pyrolysis	Moderate temperature, short-time heating	75	12	13
Slow pyrolysis	Low temperature, extremely long-time heating	30	35	35
Gasification	High temperature, long-time heating	5	10	85

heating and heat transfer rates, which requires thorough shredding of the initial biomass; strict temperature control in the pyrolysis area within a range of 420–500°C; fast extraction of vapor-gases (less than 2 s) from the pyrolysis area; and fast cooling of the pyrolysis products vapors and aerosols.

Different technological aspects of the process of biomass fast pyrolysis (drying of raw materials, heating methods and rates, reaction temperature, time spent by steam-gases in the reaction zone and their secondary splitting, separation of charcoal and ash, and extraction of liquid products) are described in survey [53].

The composition and yield of fast pyrolysis products depend on temperature conditions of the raw materials preliminary drying [54]. Kinetic modeling performed on the basis of data on weight loss during processing made it possible to suggest independent courses of fast pyrolysis reactions resulting in the formation of eight groups of products, each of which was characterized by its own boiling temperature range [55].

Liquid products obtained as a result of fast pyrolysis contain organic compounds of various classes: acids, phenols, alcohols, carbonyl compounds, and products of carbohydrates depolymerization and dehydration [55, 56]. Thus, the composition of Dynamotive bio-oil obtained through fast pyrolysis of hard wood includes formaldehyde, acetaldehyde, acetone, methanol, propanol, butanol, syringol, guaiacol and its derivatives, furfural, formic, acetic, lactic, and levulinic acids, cathechol, and many other sub-stances (about 50 compounds in total) [55]. Bio-oil can find application both as a fuel and a source for obtainment of valuable chemical substances.

Vacuum pyrolysis (530°C, 40 kPa) of soft wood bark makes it possible to obtain resins, which can be later separated into water-soluble and water-insoluble components through centrifugation [57–59]. The upper layer (~16 wt %) contains insignificant quantities of water and solids, the products contained in this layer are characterized by a high calorific capacity. The lower layer is similar to bio-oil with regard to its properties with the exception of a higher water and ash content.

Fast pyrolysis of biomass can be considered one of the major ways to obtain liquid fuels and various chemical substances suitable for further processing from the source biomass. Applicability of fast pyrolysis is limited by the necessity to use shredded and fractionated raw materials. Differences in physical properties of plant raw materials and their chemical nonuniformity hinder the creation of a universal fast pyrolysis technology.

CONCLUSIONS

The use of biomass as a raw material for obtainment of products for subsequent chemical processing is becoming a more and more promising direction for development of fuel technologies and organic synthesis, especially within the framework of modern concepts of production facilities for complex processing of bioresources.

Methods of thermal conversion of wood that are considered the most promising are liquefaction in formic acid and phenol medium and fast pyrolysis. In order to identify priority areas for energy use of wood it is necessary, among other things, to evaluate effectiveness of the technologies under consideration in terms of energy expenses for preparation of the raw materials and performance of the process and, as a consequence, to assess profitability of the production.

ACKNOWLEDGMENTS

This work is performed with financial support of the Russian Foundation for Basic Research (grant no. 10-03-92500) and the U.S. Civilian Research and Development Foundation (grant no. RUC1-2989-ST-10).

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