



Research review paper

A review of thermal–chemical conversion of lignocellulosic biomass in China

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ABSTRACT

Biomass, a renewable, sustainable and carbon dioxide neutral resource, has received widespread attention in the energy market as an alternative to fossil fuels. Thermal–chemical conversion of biomass to produce biofuels is a promising technology with many commercial applications. This paper reviewed the state-of-the-art research and development of thermal–chemical conversion of biomass in China with a special focus on gasification, pyrolysis, and catalytic transformation technologies. The advantages and disadvantages, potential of future applications, and challenges related to these technologies are discussed. Conclusively, these transformation technologies for the second-generation biofuels with using non-edible lignocellulosic biomass as feedstocks show prosperous perspective for commercial applications in near future.

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1. Introduction

Due to limited fossil fuel reserves and strict environmental regulations, there is a growing interest in the production of biofuels and the extraction of energy from biomass as a means of sustainable development in many countries (Demirbas, 2008). In China, there is an abundant quantity of biomass resources. Approximately 0.73 billion tons of agricultural residues are produced per annum, which is equivalent to 12,000 trillion kJ of energy. Furthermore, there is 37 million m³ of forest residues in China containing 580 trillion kJ of energy (Leung et al., 2004). Energy has long been obtained through direct combustion of biomass, primarily commercialized in China for electricity generation. However, this direct burning has led to low energy efficiency and significant environmental pollution despite the development of sophisticated techniques for combustion ovens. As an alternative, conversion of biomass to high quality bio-products and energy produced by advanced means other than combustion could partially substitute petroleum-based fuels and decrease greenhouse gas emissions. For this reason, R&D on first- and second-generation biofuel technologies and processes has been carried out in recent years. First-generation biofuels include: ethanol and butanol, which are produced by hydrolysis or fermentation of starches or sugar; biodiesel, which is produced by transesterification of plant oils with methanol; and gasoline and diesel which is produced by refinery of catalytic hydrotreating process. Limitations of first-generation biofuels include direct competition with food production and the utilization of only a portion of the total biomass (Hamelink and Faaij, 2006). In China, the production of ethanol from corn and the production of biodiesel from vegetable oils could not fulfill energy requirements since the corn and vegetable oils production capacity serves as food for 1.3 billion people.

Second-generation biofuels use non-edible feedstocks of lignocellulosic biomass, such as, crop residuals (e.g. corn stalks or rice husks), woody crops, or energy grasses. The development of technology for converting lignocellulosic biomass to bio-products and energy has attracted significant attention in recent literatures. For example, the Chinese government issued “The Law of People’s Republic of China Renewable Energy” in 2006 (People’s Congress, 2005), and “The medium and long period programming for renewable energies” was initiated by the Chinese government stressing that the electric power capacity from biomass will be 3×10^7 KW, and the amount of liquid bio-fuels will be 1×10^7 tons by the year 2020, both of which significantly promoted the development of second-generation biofuels under the funding of Ministry of Science and Technology, Ministry of Agriculture, and Chinese Academy of Sciences.

Methods of thermal–chemical processing of lignocellulosic biomass, such as gasification, pyrolysis or catalytic transformation, are simple and efficient with promising commercial applications. In this paper, advances in research and development on the thermal–chemical conversion of biomass in China are introduced. The current status and future prospects of technologies are also compared and discussed.

2. Gasification

In China, the R&D of biomass gasification technology began fifty years ago and has rapidly advanced since the 1980s. Many gasifiers such as, ND series, XFL series, GSQ-110, QL50, QL60, have been commercialized (Sun et al., 2011a,b). The produced gasses have been widely used in many applications including power generation, household cooking with pipe delivery, heating and steam supply by boiler

combustion, H₂ production via pressure swift absorption, and liquid fuels and chemicals production via Fischer–Tropsch (FT) synthesis. Different kinds of gasification methods have been developed such as, the production of low heating-value fuel gas (4–6 MJ/Nm³) by air gasification, medium heating-value fuel gas (12–15 MJ/Nm³) by oxygen-rich gasification, and hydrogen-rich fuel gas (H₂ content of 30 vol.%–60 vol.%) by oxygen-containing steam or steam gasification.

2.1. Gasifier

2.1.1. Fixed-bed gasifier

In the 1980s, the updraft fixed-bed gasifier was designed to produce fuel gas for concentrative cooking supplies and for heating in the Heilongjiang and Fujian province of China. The maximal capacity of one unit reached 6.3×10^6 KJ/h, but this kind of gasifier produced a low heating-value fuel gas containing large amounts of tar which inhibited its application. Consequently, no updraft fixed-bed gasifiers are currently in use in China.

The downdraft fixed-bed gasifier was developed through modification of the updraft fixed-bed gasifier. In this type of gasifier, the feedstocks and gasification agents are fed at the top, and the produced fuel gas exits at the bottom. Hot carbon at the bottom of gasifier is used for particle filtration and tar cracking, so relatively clean fuel gas can be produced without the need for an additional complicated downstream cleaning unit. In China, small-scale units of this type with a capacity of below 1 MW have been commercialized in several fields such as electricity generation by internal combustion engines, and household cooking with pipe delivery.

The use of a cross-flow gasifier was also investigated to further improve the performance of fixed-bed gasifiers. Due to complicated structure design and operation, this type of gasifier is still in development.

Fixed-bed gasifiers offer advantages of a single structure, easy operation, low cost and excellent biomass feedstocks adaption; however, both the capacity per unit and heating-value of the produced fuel gas are low, thereby prohibiting large scale applications.

2.1.2. Fluidized-bed gasifier

With rapid advancements in biomass gasification technologies and applications, the need became apparent for the development of a large-scale gasification plant. Difficulties involving the scale-up process of fixed-bed gasifiers resulted in the development of fluidized-bed gasifiers. China has made many developments on the R&D of fluidized-bed gasifiers throughout the past twenty years. A 1 MW biomass gasification and power generation plant was set up in 1998 adopting the fluidized-bed gasifier designed by the Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (GIEC/CAS) (Wu et al., 2002). Since then, China has increased interest in the R&D of fluidized-bed gasification technologies. Many Chinese companies such as rice mills and timber mills, have set up biomass power plants to convert their cheap residues (rice husk or wood sawdust) to fuel gas used for electricity generation or heat supply. In recent years, almost thirty plants with a combined total capacity of over 40 MW have been established in China and several Southeast Asian countries. The innovations in fluidized-bed gasification have focused on unit enlargement, design of gasifier internal structure, and the abatement of biomass tar within and downstream of the gasifier (Leung et al., 2004).

Due to similarities in the technologies of biomass gasification and coal gasification, research in China has increased on coal/biomass

co-gasification in recent years. The biomass/coal ratio is usually kept below 0.5 to maintain excellent fluidization of biomass and coal particles in the fluidized-bed gasifier. The performance of mixed feedstock gasification, as determined through carbon conversion and the heating value of fuel gas, was found to be better than that of biomass or coal gasification indicating co-promotion effects between the two kinds of feedstocks.

In developed countries, biomass resources are concentrated, and large gasifiers are suitable for dealing with these abundant biomass feedstocks. However, the distribution of biomass resources in China is dispersed, promoting the development of medium-scale gasifiers (below 10 MW). The key goals in the technological advancement of gasification are to improve tar abatement and efficiency.

2.2. Upgrading and application

2.2.1. Syngas production

The raw fuel gas produced by gasifiers contains large amounts of tar and particles which inhibit its use in gas turbines, solid oxide fuel cells, and FT synthesis. In China, many biomass gasification plants adopt water scrubber technologies to remove tar and particles in the raw fuel gas. This cleaning process was found to be ineffective in tar removal, so the cleaned fuel gas could only be used for power generation by internal-combustion engines or for household cooking with pipe delivery. Corrosion and blockages of pipes and equipment are still serious concerns for long-term runs. Many methods have been developed to solve this problem in the last twenty years, including modifying the gasifier structure and downstream catalyst beds.

GIEC/CAS designed a pilot system to produce clean syngas in 2005. The system contained a fluidized-bed gasifier with a downstream charcoal cracking stove, and pine sawdust at 500 kg_{dry}/h was used as a feedstock. The raw syngas produced by the gasifier was upgraded by thermal cracking and filtration in the downstream cracking stove. A temperature of 1000 °C was maintained in the stove by burning charcoal. The tar content in the clean syngas decreased to a level of 1 g/Nm³. However, the large amounts of charcoal consumed in the cracking stove decreased the gasification efficiency (Wu et al., 2010a).

Syngas with low tar content can be produced by coupling a pyrolyzer and fixed-bed gasifier (Li et al., 2009d). A pilot-scale coupling system (Fig. 1) was designed by Shandong Province Institute of Energy Conversion, China. The composition of the product syngas was H₂

25–38 vol.%, CO 25–38 vol.%, CO₂ 16–25 vol.%, CH₄ 0–2 vol.%, O₂ < 1 vol.%, C₂₊ < 0.05%, N₂ 8–10 vol.%, and H₂/CO = 0.98–1.17. The tar content in the bio-syngas was below 20 mg/m³.

Increasing the gasifier height or partitioning a second oxygen flow stream into the gasifier can promote tar abatement in the gasifier, and following catalytic reforming of the biomass raw fuel gas over nickel based catalysts, can deeply convert the tar into H₂ and CO (Wang et al., 2006). Recently, GIEC/CAS set up a novel pilot-scale biomass gasification-reforming system (Fig. 2). The system was composed of a biomass feeder, fluidized-bed gasifier, downer reactor, reformer, water scrubber, and synthesis gas tank. Pine sawdust was gasified in the fluidized-bed gasifier with air, oxygen and steam. The obtained raw fuel gas passed through a downer reactor to eliminate tar content by thermal cracking and to separate coking particles. It was then fed into a reformer packed with highly stable nickel-based catalysts to convert the biomass tar into H₂ and CO. With the addition of steam into the gasifier and reformer, an ideal syngas product (H₂/CO ratio of 1.4 and tar content of 15 mg/Nm³) was obtained. The cold gas efficiency was increased to 82% (Wang et al., 2006).

2.2.2. H₂ production

In modern industry, hydrogen is generally produced by steam reforming of natural gas. Biomass gasification (addition of steam as gasification agent) can also generate H₂-rich fuel gas from which pure hydrogen can be produced through pressure swing adsorption technology. However, the small scale of biomass gasification for hydrogen production results in high costs, so currently, no plants in China produce hydrogen by this method. However, the H₂-rich fuel produced through biomass gasification has an H₂/CO ratio of above 1.0 and therefore can be used as syngas for FT synthesis processes which do not require separation and purification of H₂ from mixed gasses. Research in China is focusing on how to increase the H₂ content by high temperature steam gasification. The pure steam gasification of biomass can increase H₂ content to a level of 60 vol.%, but continuous operation of a gasifier is difficult. Oxygen-rich steam gasification can produce H₂-rich fuel gas with H₂/CO ratios of 1.5 by operation in a self-thermal model which can improve the gasification efficiency to 82%.

At Xi'an Jiaotong University, research on supercritical water gasification (SCWG) technology is underway. The SCWG technology can produce fuel gas with an H₂ content of above 50 vol.% under the conditions of 374 °C and 22 MPa. This process can convert almost 100% of

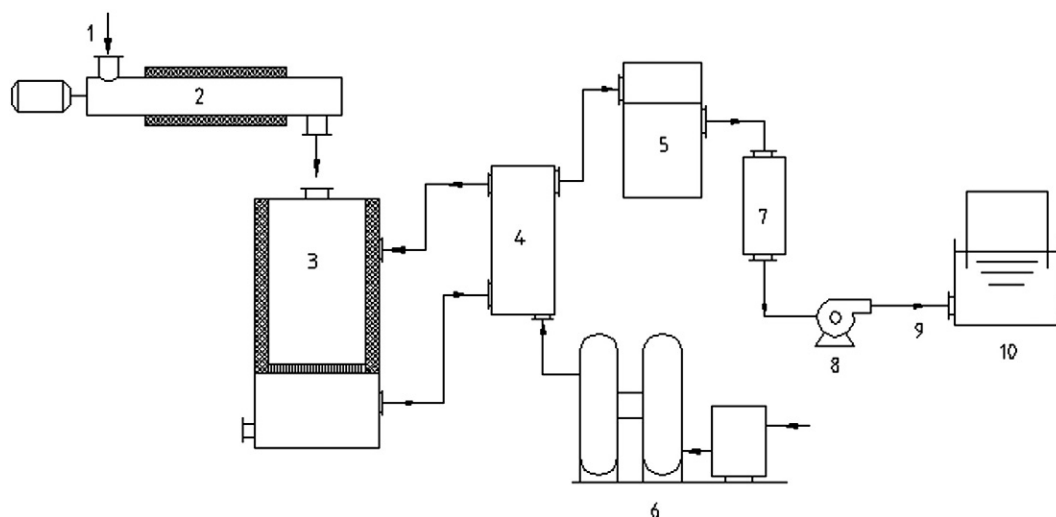


Fig. 1. Schematic diagram of syngas production by coupling of pyrolyzer and fixed-bed gasifier: 1—biomass inlet, 2—pyrolyzer, 3—gasifier, 4—heat exchanger, 5—bag filter, 6—PSA unit, 7—cooler, 8—roots blower, 9—syngas flowmeter, 10—syngas tank.

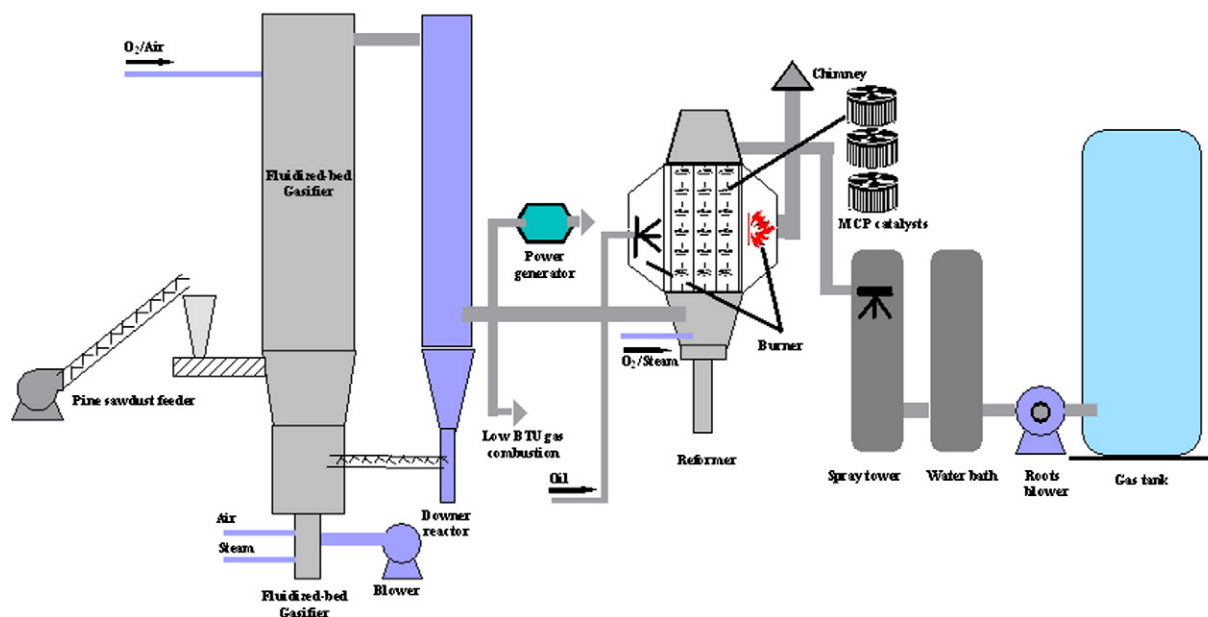


Fig. 2. Schematic diagram of syngas production by biomass gasification-reforming system.

the biomass feedstock into gasses with only small amounts of tars and solid residues. The reaction temperature and time-on-stream have a significant impact on the H_2 production (Hao et al., 2003; Lu et al., 2008). Due to the rigorous conditions required for this technology, further developments are required in the future.

2.2.3. Electricity generation

Technologies for power generation from biomass resources have been rapidly developed since 1990 and have been commercialized in China and Southeast Asian countries. Currently, there are four different technologies that have been developed: biomass gasification & power generation (BGPG), biomass integrated gasification combined cycle and power generation (BIGCCPG), biomass combustion and power generation (BCPG), and biomass/coal co-firing and power generation (BCCPG).

R&D of BGPG technologies began in China as early as the 1960s. The first integrated system was a plant performing rice husk gasification for power generation of 60 kW by an internal-combustion engine. This novel engine was designed by modifying the diesel engine to meet the requirements of biomass fuel gas which has a low heating value of 4–6 MJ/Nm³. Before 1998, 160 or 200 KW BGPG systems were adopted widely in Chinese rural areas with rice husk as feedstocks. Since 1998, the MW-scale BGPG system has been developed by GIEC/CAS. The circulating fluidized-bed gasifier was developed for relatively large scale systems. An efficiency of 18% has been obtained for this MW-scale BGPG system which has been widely used as a self-supplied power plant by rice mills and timber mills in China (Wu et al., 2002; Yin et al., 2002).

In order to improve the energy efficiency and market competitiveness, the BIGCCPG technology was developed and a demonstration plant with a power output of 5.5 MW was set up in the Jiangsu Province of China by the end of 2005. Long-term test results showed that the energy efficiency reached 26–28% with an equipment investment of 1200 USD/KW (Wu et al., 2009a).

Since “The Law of Renewable Energy” was issued in China, the government has given many incentives for biomass-based power. The purchasing price of biomass-based electricity is higher than that of coal-based electricity which has attracted many power companies to enter into the biomass-based market. By the end of 2006, 39 BCPG projects had been authorized for construction in which the

technology was imported from the BWE Company in Denmark. The total installation capacity was 1284 MW. This imported BCPG technology has been effective for the combustion of forest residues but not for corn stalk feedstocks that are abundant in China. The major reason may be attributed to significant amounts of ash present in corn stalk, which leads to the blockage and alkali metal corrosion of units.

Due to both the difficulties collecting biomass feedstocks in large scale and the status of coal power factories with installation capacity of above 10 billion KW in China, the BCCPG technology was developed for co-firing of biomass and coal. This technology alleviated the difficulties associated with stable operation in large power plants by directly adding small amounts of biomass to coal feedstocks. Currently, most of the large biomass power plants in China have adopted the BCCPG technology.

2.2.4. Liquid fuels and chemicals synthesis

Biomass to liquid fuel (BTL) is an indirect liquefaction technology in which biomass is firstly gasified to raw syngas and subsequently converted to a high-quality designed fuel over different FT catalysts. BTL technologies represent a promising option for biofuel production. The obtained biofuels can be different from fossil fuel substitutes, such as gasoline, diesel, kerosene and oxygenated fuels (methanol, DME and mixed alcohols). Compared with direct biomass liquefied products like pyrolysis oil, BTL fuels are ultra-clean without S and N contaminants allowing for easy coupling with pre-existing fossil fuel supply systems and their use in a broad range of applications.

R&D on fluidized-bed biomass gasification has been carried out in GIEC/CAS for over 3 decades, and more than 20 biomass integrated gasification combined with cyclic power generating plants of 3–10 MW have been built. Based on the mature fluidized-bed biomass gasification technology in GIEC/CAS, 100 tons/a-scale and 1000 tons/a-scale integrated Bio-DME synthesis systems from biomass gasification were set up in 2006 and 2009, respectively (Li et al., 2009d).

In the 100 tons/a-scale bio-DME pilot plant, the bio-syngas was produced by the coupling of pyrolysis and gasification technologies as mentioned above. After removal of S, Cl, O₂ and partial CO₂ in the bio-syngas, the product was directly converted to DME over a Cu–Zn–Al/HZSM-5 catalyst in a fixed-bed reactor at conditions of 4.2–4.4 MPa and 260–270 °C. The unconverted syngas can be recycled for DME synthesis or combusted in a gas turbine for electricity generation.

Compared with industrial syngas ($f = (H_2 - CO_2)/(CO + CO_2) = 2.0$), the bio-syngas ($f = 0.548-0.662$) was found to be CO-rich and CO₂-rich. After once-through DME synthesis, the CO conversion, DME selectivity, and DME yield reached 73–82%, 70–74%, and 124–203 kg/m³h respectively.

Based on the results of the 100 t/a-scale system, a 1000 t/a-scale demonstration plant was set up in November, 2008. The system includes four units: (1) gasification unit for converting solid biomass to raw bio-syngas; (2) raw bio-syngas cleaning and composition adjustment to remove contaminants (flying ash, tar, Cl, S, NH₃ and small char particles) in the raw bio-syngas. Contaminant removal is necessary in order to avoid poisoning and deactivating of the catalysts in the downstream units. The bio-syngas composition should be adjusted to meet with the requirements of the DME synthesis; (3) Once-through DME synthesis unit; (4) DME refining unit by extraction, adsorption and distillation. In order to increase the total efficiency, a waste heat boiler, gas engine, or steam turbine were integrated in the demonstration plant to generate heat or electricity (Li et al., 2010b).

The performance results of the 1000 tons/a-scale demonstration plant were as follows: a bio-DME production rate of 6–7 t_{biomass}/t_{DME}, biomass gasification efficiency ≥82%; once-through CO conversion ≥70%; DME selectivity (DME/DME + other organic products) ≥90%; steam and electricity self-sufficiency; total efficiency of the system ≥38%. The 10,000 tons/a-scale bio-DME production cost with or without a feedstock subsidy is estimated to be ¥1968/ton and ¥2868/ton respectively in China. Due to the limitation of biomass feedstock collection costs, large and disperse commercial plants with a capacity of 10,000 tons/a bio-DME are suitable in rural areas (Li et al., 2010b; Lv et al., 2009).

3. Pyrolysis

Pyrolysis is a process that converts biomass at temperatures around 450–550 °C in the absence of oxygen to liquid (bio-oil), gaseous, and solid (char) fractions. The use of catalysts or additives to improve the yield and quality of gas or liquid fuels from biomass is common. Extensive fundamental studies have been carried out to explore the wide range of conventional and unconventional catalysts. In the following section, state-of-the-art technologies and developments concerning production, upgrading, and utilization of bio oil, with a special focus on different catalysts, is introduced. Bio oil can be used in further conversion processes, such as efficient power generation gasification for syngas production and as an alternative fuel for vehicles.

3.1. Production of bio-oil

3.1.1. Fast pyrolysis

Fast pyrolysis, which uses a high heating rate and short residence time, can obtain increased bio-oil yields (Jung et al., 2008). Fluidized-bed reactors have many advantages for fast pyrolysis of biomass, such as simple structures, high production capacities, favorable conditions of heat and mass transfer, and convenient operation. Zhejiang University set up a fluidized-bed flash pyrolysis reactor operating at atmospheric pressure and 450–600 °C. Nitrogen was used as the fluidizing medium and was fed continuously at a rate of 20 kg/h. The biomass feedstock contained Chinese fir, Manchurian ash, padauk wood and rice straw. The results showed that padauk wood had the best characteristics for producing bio-oil, and that high temperatures hindered bio-oil production due to secondary cracking. However, lower temperatures led to incomplete decomposition of the biomass feedstock and therefore decreased bio-oil yield (Wang et al., 2005).

Using a circulating fluidized-bed (CFB) as a reactor, an integrated facility was developed for the fast pyrolysis of biomass in GIEC/CAS. It was reported that the main chemical processes in the CFB could be

modeled. The bed was divided into zones corresponding to the pyrolysis and secondary reactions. The pyrolysis of wood powder was carried out by varying the bed temperature, particle size of wood powder, and the feeder position. Two main conclusions found were: (1) higher temperatures and longer residence times contributed to secondary reactions leading to less liquid yield; (2) lower heating rates favored the carbonization reaction reducing the liquid yield. The analysis of bio-oil components showed that most of the compounds were non-hydrocarbons and alkanes. Aromatics and asphalt content were relatively low (Dai et al., 2000).

Twente rotating cone pyrolysis, a process which continuously feeds biomass at a rate of 50 kg/h, was introduced by Shenyang Agricultural University in 1995. Subsequent modifications on the rotating cone reactor were set up in Northeast Forestry University and the University of Shanghai for Science and Technology. The rotating cone pyrolysis reactor can provide higher heating rates (1000 °C), and shorter residence times of pyrolysis vapor which results in high bio-oil yields of 60 wt.%. The cone rotational frequency, particle size of the biomass feedstock, residence time of pyrolysis vapor, and pyrolysis temperature were key factors that were found to affect the distribution of pyrolysis products (Liu et al., 1997; Xu et al., 2000). Current developments in fast pyrolysis processes for bio-oil production in China are listed in Table 1.

3.1.2. Novel pyrolysis

Microwave pyrolysis is a relatively new technique that has been developed and investigated in recent decades. It is suspected that microwave heating sources will affect yield distribution in gas, liquid, and solid phases compared to conventional heating methods such as external heating by conduction, convection or radiation. In a previous study, the property of bio oil produced by microwave pyrolysis was reported to be more maltenic, less polar, and contain less sulfur and nitrogen than those obtained by conventional pyrolysis (El harfi et al., 2000). Chen et al. (2008) combined microwave heating and the use of additives to study the catalytic pyrolysis of pinewood sawdust and to investigate their effects on the composition and distribution of the fluid phases.

Vacuum pyrolysis of biomass, in comparison with other pyrolysis technologies, has several advantages: (1) short retention time and a low pyrolysis temperature prohibits side reactions, (2) higher liquid yield and quality, (3) the crude activated charcoal is less deposited and favors subsequent processing (Roy and Chaala, 2001). The process is typically carried out at 450 °C under a pressure of 15 kPa (Bridgwater and Peacocke, 2000). The ongoing research concerning typical pyrolysis technologies are reviewed in Table 2.

Table 1

Typically fast pyrolysis reactor developed in China.

University	Reactor types	Capacity
Shenyang Agricultural University	Rotating cone	50 kg/h
University of Shanghai for Science and Technology	Rotating cone	10 kg/h
Northeast Forestry University	Rotating cone	50 kg/h, 200 kg/h
Shenyang Agricultural University	Fluidized-bed	5 kg/h
Guangzhou Institute of Energy Conversion, CAS	Circulating	10 kg/h
University of Shanghai for Science and Technology	Fluidized-bed	5 kg/h
East China University of Science and Technology	Fluidized-bed	5 kg/h
Zhejiang University	Fluidized-bed	20 kg/h
Shandong University of Technology	Fluidized-bed	50 kg/h
University of Science and Technology of China	Fluidized-bed	20 kg/h, 120 kg/h
Tianjin University	Fluidized-bed	25 kg/h
Devotion group	Fluidized-bed	Products: 3000 t/a

3.1.3. Deoxy-liquefaction

Deoxy-liquefaction of different biomass feedstocks, including water hyacinth, legume straw, corn stalk, cotton stalk, wheat straw, and soybean stalk, were investigated by Wang et al. (2008). Generally, the HHV (higher heating value) of bio-oil obtained by biomass deoxy-liquefaction was found to be greater than 40 MJ/kg. The H/C molar ratio was found to be higher than 1.5, and the oxygen content was determined to be lower than 6 mol%. Alkanes, cycloalkanes, and aromatic hydrocarbons were the main products in the bio-oil. The properties of the bio-oil are close to those of petroleum except for the oxygen content. Bio-oil obtained from deoxy-liquefaction of soybean possessed an H/C molar ratio of 1.9 and a higher heating value of 44.22 MJ/kg. Bio-oil with an H/C molar ratio of 2.0 and HHV of 46.95 MJ/kg was produced after bathing with a 1% NaOH solution by refluxing. The bio-oil was further distilled, and the composition of the distillate at 240–350 °C was found to be similar to that of diesel oil (Chen et al., 2010; Li et al., 2008; Lu et al., 2009; Wang et al., 2008). Wu et al. (2009b) produced alkanes (C₇–C₂₉) from different parts of a poplar tree (leaves, bark and wood) via direct deoxy-liquefaction. The compositions of the obtained oils were found to vary. The oil from leaves was rich in hydrocarbons (alkanes: C₇–C₂₉; aromatics) and poor in phenolics while oil from wood was rich in phenolics and poor in hydrocarbons. The HHVs of the produced oils were 45.47, 40.18 and 34.92 MJ kg⁻¹ respectively.

The effects of solvent addition on the pinewood liquefaction process have been investigated. The highest conversion rate was obtained when acetone was employed as a liquefaction solvent, and the highest oil yield was found to be 26.5 wt.% using ethanol in the liquefaction process. The product distribution was also strongly affected by the solvent. For example, the major compounds were 2-methoxy-phenol, 1-PA acid and 4-hydroxy-3-methoxy-benzeneacetic acid in the case of water liquefaction processes while the composition of oil from acetone liquefaction processes consisted mainly of 1-PA acid, 2-methoxy-furan, and 4-methyl-1,2-benzenediol-1- (4-hydroxy-3-methoxy-phenyl)-ethanol. It was therefore concluded that employing different solvents can change the distribution and relative abundance of the produced compounds (Liu and Zhang, 2008).

Liquefaction of sawdust with the addition of syngas was performed at 200–350 °C using an initial, cold syngas pressure range of 2–10.3 MPa and a reaction time of 10–60 min. It was found that a hydrogen donor solvent exhibited desirable effects compared to both non-hydrogen donor solvents and no solvent at all. The ability for sawdust liquefaction was found to be greater than what was observed using gaseous hydrogen. Comparing various atmospheres, H₂ displayed higher activity than syngas but both were better than Ar and CO. Using a CO environment negatively impacted activity (Wang et al., 2007a). A 1 wt.% Mo catalyst was added in order to produce more liquid fuel during the sawdust liquefaction under an initial syngas pressure of 2.0 MPa and temperature of 300 °C. It was found that gaseous hydrogen and the addition of the catalyst did not produce significant effects in the absence of solvent. Consequently, a hydrogen-donor solvent plays an important role in sawdust liquefaction (Wang et al., 2007b).

In order to investigate the effects of catalysts on the biomass liquefaction process, paulownia was liquified in hot, compressed water with and without the presence of catalysts such as Fe and Na₂CO₃. Liquefactions were conducted under vacuum and at temperatures of 280–360 °C for 10 min. It was found that heavy oil products increased when Na₂CO₃ and Fe were added into the reactor. The maximum heavy oil yield was 36.34 wt.% using an Fe catalyst at 240 °C, and the minimum solid residue yield was obtained when Na₂CO₃ was employed as catalyst. Reaction temperature significantly influenced the process of biomass liquefaction, where the yield of heavy oil initially increased with temperature until the onset of secondary reactions resulted in a decrease in yield. The major compounds were found to be phenol derivatives, ketones, carboxylic acid esters, benzene derivatives and long-chain alkanes, as well as aldehydes and its derivatives (Sun et al., 2010; Sun et al., 2011a,b).

3.1.4. Super-critical fluids liquefaction

Recently, super-critical fluids have gained increased attention. Super-critical fluids possess unique transport properties such as gas-like diffusivity and liquid-like density, and they have excellent miscibility, thereby providing a single-phase environment for reactions that would not occur under conventional conditions. Super-critical fluids have the ability to dissolve biomass materials which would not be normally soluble in either liquid or gaseous phases of the solvent, and consequently, they promote liquefaction reactions (Xu and Etcheverry, 2008).

Without the presence of a catalyst, bio-oil yields were in the range of 35.4–45.3 wt.%. It was believed that FeS would be a good catalyst for the liquefaction of *Spirulina* microalgae. It was determined that the addition of a 5–7 wt.% FeS catalyst could promote bio-oil production and suppress the formation of residue. The obtained bio-oil had higher heating values than the crude *Spirulina* microalgae (Huang et al., 2011). The sub- and supercritical liquefaction of rice straw to produce bio-oil with a mixed solvent (ethanol–water and 2-propanol–water mixture) was studied at conditions of 260–350 °C and 6–18 MPa. The results indicated that using a solvent mixture can promote the conversion of rice straw and inhibit the formation of low-boiling point materials. The highest oil yield of 39.7 wt.% was obtained using a 2-propanol/water volume ratio of 1:1 at 300 °C. At this ratio, the oxygen content in the oil was 27.29 mol% but decreased with an increase in the ratio of hydrogen donor solvent (ethanol and 2-propanol). An increase in heating value was found to correspond with decreasing the amount of hydrogen donor solvent (Yuan et al., 2007). The critical liquefaction of a sub- and supercritical 1,4-dioxane–water mixture was also studied at 260–340 °C. The results indicated that the synergistic capability of the 1,4-dioxane–water mixture could allow a greater decomposition of the tubular structure of lignocelluloses. Moreover, it was found that deoxygenation and decarboxylation reactions may occur during the liquefaction of rice straw with sub- and supercritical 1,4-dioxane–water mixture (Li et al., 2009c).

Alkaline solutions, such as Na₂CO₃ and K₂CO₃, have been widely employed as catalysts in the biomass direct liquefaction process to suppress the formation of char while enhancing the yield of liquid products. For example, Shao et al. (2007) pyrolyzed bamboo in supercritical methanol using K₂CO₃ as a catalyst. The results indicated that a temperature range of 270–280 °C is suitable for this process. The liquefaction rate was found to be 34.3 wt.%. A K₂CO₃ catalyst was found to promote the pyrolysis of bamboo, and a liquefaction rate of 46.3 wt.% was achieved under the same conditions. The pyrolysis products of bamboo included alcohols, esters, ketones and ethers. Zhong and Wei (2004) investigated the aqueous liquefaction of *Cunninghamia lanceolata* and *Fraxinus mandshurica* using a temperature range of 280–360 °C. The results revealed that the lignin content had an obvious effect on the yield of liquefaction products in non-catalytic processes. Addition of K₂CO₃ was found to significantly reduce the residue yield of all the woods tested. Zou et al. (2010) investigated the hydrothermal liquefaction of the microalgae species *Dunaliella tertiolecta* cake using 5% Na₂CO₃ as a catalyst. The heating value of the liquid product obtained at optimal conditions was 30.74 MJ/kg.

The effect of catalysts on aqueous liquefaction of straw was also investigated using a high-pressure autoclave and sub-critical water (T = 300 °C, P = 18 MPa, t = 5 min). It was found that an appropriate amount of ZnCl₂ could increase the output of the bio-oil as much as 32.90%. Addition of Na₂S was able to improve the HHV of the bio-oil to a maximum of 34.05 MJ/kg. When catalysts composed of ZnCl₂ and Na₂S were added, both the output and HHV of the bio-oil achieved maximum values of 33.85% and 34.42 MJ/kg, and the residue of reaction was minimized (Xie et al., 2008).

3.2. Upgrading of bio-oil

Bio oil produced from pyrolysis is complex in chemical composition and highly unstable in terms of chemical properties, physical

Table 2
Current research of typical pyrolysis technologies in China.

Technology	Feedstock	Catalysts	Conditions	Conclusions	References
Microwave pyrolysis	Corn stover and aspen wood	Metal oxides and chloride salts (K ₂ Cr ₂ O ₇ , Al ₂ O ₃ , KAc, H ₃ BO ₃ , Na ₂ HPO ₄ , MgCl ₂ , AlCl ₃ , CoCl ₂ , and ZnCl ₂)	100 g sample, 20 min, 450–550 °C,	KAc, Al ₂ O ₃ , MgCl ₂ , H ₃ BO ₃ , and Na ₂ HPO ₄ were found to increase the bio-oil yield. MgCl ₂ is effective in improving the product selectivity of the microwave-assisted pyrolysis.	Wan et al. (2009)
	Pine wood sawdust	NaOH, Na ₂ CO ₃ , Na ₂ SiO ₃ , NaCl, TiO ₂ , HZSM-5, H ₃ PO ₄ , Fe ₂ (SO ₄) ₃	Microwave heating at ca. 470 °C under dynamic nitrogen atmosphere.	Sodium compounds have positive effect on acetol formation in the order of NaOH > Na ₂ CO ₃ > Na ₂ SiO ₃ > NaCl. TiO ₂ goes against the formation of acetol, HZSM-5 has no marked effect on acetol formation. Fufural and 4-methyl-2-methoxy-phenol are the dominant organic components identified in the liquid products in presence of H ₃ PO ₄ and Fe ₂ (SO ₄) ₃ .	Chen et al. (2008)
Vacuum pyrolysis	pine sawdust	Mo–10Ni/g-Al ₂ O ₃	Boiler with i.d. 30 mm, height 120 mm. 300 g, 3.5–4 kPa, 400–600 °C.	The maximum amount of bio-oil of total liquid product was obtained between 300 °C and 400 °C with 47.81 wt.%. At the temperature of 500 °C and in the pine sawdust sized in 170–250 μm, maximum bio-oil yield was obtained.	Zhang et al. (2010a)
		–	–	–	Xu et al. (2009)
Flash pyrolysis	Manchurian Ash; China Fir; Padauk Wood; Rice straw	–	Fluidized-bed with a diameter of 80 mm, height of 700 to 1200 mm, 3 kg/h, 1 atm, nitrogen, 450–700 °C.	Padauk Wood has the highest bio-oil yield (55.7%), followed by China Fir (53.9%), Manchurian Ash (40.2%) and Rice Straw (33.7%). Modeling result points 500 °C as the recommended dense bed temperature for bio oil production.	Wang et al. (2005)

consistency, and combustion characteristics, which impose many obstacles on its applications. Consequently, several techniques have been developed to upgrade bio oil, including: hydrodeoxygenation (HDO) (Bunch et al., 2008), catalytic cracking, emulsification (Ikura et al., 2003), esterification, and steam reforming.

Due to high oxygen content (35–40%) (Zhang et al., 2007a), bio-oil possesses a poor volatility, a high viscosity, a low heating value, and chemical instability. HDO processes were the dominant methods in removing oxygen as water and/or carbon oxides under a high hydrogen pressure (4–10 MPa) and at moderate temperature (300–500 °C). Conventional hydrotreating catalysts such as sulfided CoMo/Al₂O₃ or NiMo/Al₂O₃ can be used in these processes (Xu et al., 2010a; Zhang et al., 2010b). Xiong et al. (2009) explored a new method for upgrading by esterification of organic acid in bio-oil using acidic, ionic, liquid catalysts. Catalytic cracking is a conventional method used to convert high molecular weight oil components to lower molecular weight compounds which can be blended for use as fuel (Li et al., 2009b). Common catalysts used include: HUSY, REY and HZSM-5 zeolite supported on g-Al₂O₃, two industrial FCC catalysts labeled as MLC-500 and CIP-2 (Lu et al., 2007); H-Beta-25, H-Y-12, H-ZSM-5-23, Al-MCM-41, Cu-Al-MCM-41, FCC, SBA-15, Al-SBA-15, MCM-1, MCM-2, MCM-3, Cu-MCM, Fe-MCM, and Zn-MCM (Peng et al., 2010). In recent years, several research institutions have studied the steam reforming of bio-oil, as well as the effects of model compounds for hydrogen production on feedstock (Zhang et al., 2007a), reactor design (Wu et al., 2008), and reforming catalysts (Zhang et al., 2007b).

Bio oil is a complex, highly oxygenated mixture containing a large number of macromolecules including esters, ethers, aldehydes, ketones, phenols, and organic acids. The complexity of bio oil has led to difficulties in identifying the upgrading mechanism and catalyst performance. Therefore, several model compounds were adopted to evaluate the upgrading process (Table 3).

3.3. Utilization of bio-oil

Bio oil possesses several distinct properties compared to fuel oil. The low heating values of bio oils results in difficulty of ignition, instability when subjected to relatively high temperatures for long periods, and self-polymerization leading to the plugging of combustion systems. After several attempts to develop suitable refinery methods to improve its physical–chemical characteristics, the utilization of bio oil

has progressed and is introduced in this section with a special focus on its direct use in kilns, boilers, gas turbines, and diesel engines.

As a liquid fuel, bio-oil can be used independently or mixed with fossil fuels in boilers for heat and power generation (Zheng and Kong, 2010). Liu et al. (2008) focused primarily on spray combustion of pure, fast pyrolysis bio-oil from rice husk in a combustion system with considerations in two areas: 1) the combustion temperature distribution as a function of time and location; and 2) the emission levels of CO, NO_x, SO_x and O₂ as a function of combustor operating conditions. However, Liu and Zhang (2008) reported the difficulties of ignition for pure bio-oil in small kilns and suggested that applications of bio-oil in combustion chambers need to modify the nozzle and adjust the spray velocity. A polar solvent, such as methanol or ethanol, is often added to improve the volatility and heating value and to decrease the viscosity and acidity. By adding methanol or ethanol into bio-oil, the ease of ignition improves and the temperature increases, thereby reducing the formation of CO and NO (Liu and Zhang, 2008).

Additionally, bio-oil is able to drive diesel engines for power generation and can also be directly applied to gas turbines. Tan et al. (2008) proposed that co-firing bio-oil and fossil fuels in boilers and gas turbines is most likely to be applied in large-scale systems, and its combustion in diesel engines is a promising technology. A previous study (Lopez Juste and Salva, 2000) introduced combustion of wood derived fast pyrolysis oil and mixtures with ethanol in a gas turbine, and concluded that the combustor performance with mixtures of 80% bio oil/ 20% ethanol is similar to the combustion performance with JP-4. Xu et al. (2010b) mixed the emulsified bio oil (up to 10%) with 0# diesel (China standard GB252-2000) at 54–56 °C and an emulsifying agent up to 0.5 wt.%. The lubrication performance of the mixture was studied, and it was found that emulsified bio oil possessed a better friction reduction performance but poorer wear resistance than 0# diesel.

4. Catalytic transformation of Lignocellulose

Lignocellulose is a complex, macromolecular polymer composed through the cross-linking of C–O and C–C bonds in its three primary constituents: cellulose, hemicellulose, and lignin (Martinez et al., 2005). To separate the primary constituents and keep their respective structural units intact, cracking lignocellulose macromolecules under physical, chemical and biological pretreatments can be performed

Table 3
Review of state-of-the-art technologies for upgrading of bio-oil.

Upgrading methods	Objective	Catalysts	Conclusions	References
Hydrotreating	Rice husk	In sub- and super-critical ethanol with HZSM-5	HZSM-5 with low Si/Al ratio could facilitate cracking of heavy components of crude bio-oil effectively. The amount of heavy components decreased.	Peng et al. (2009)
Hydrodeoxygenation	Bio-oil obtained in a fluidized bed unit (5 kg/h)	Sulfided Co–Mo–P catalyst in an autoclave using tetralin as solvent	Optimum condition is: temperature 360 °C, reaction time 30 min and cold hydrogen pressure 2 MPa.	Zhang et al. (2005)
Hydrodeoxygenation	Phenol as model compound	On Ni and Mo amorphous bimetallic catalysts	The highest conversion of phenol over Ni–Mo–B amorphous catalyst was almost 100%. The total selectivity of oxygen-free products up to 93.1% with a selectivity of 3.2% aromatics over Co-promoted Ni–Mo–B catalysts.	Wang et al. (2010a)
Hydrodeoxygenate	Guaiacols, syringols, 4-n-propylphenol, and 2-methoxy-4-n-propylphenol etc.	A series of active carbon supported noble metal catalysts, such as Ru/C, Pd/C, Rh/C, Pt/C	The conversion of the mixture of monomers and dimmers obtained in the degradation of wood lignin was very high (conversion of monomer 94.0%, and dimer 82.3%).	Yan et al. (2010)
Esterification	Converting furfural to pentane Acetic acid as a model compound	Over the Ni-based bifunctional catalysts in water 0.06MoNi/γ-Al ₂ O ₃ catalysts	Conversion of furfural over 14%Ni/SiO ₂ –Al ₂ O ₃ catalyst was 62.99% under 140 °C and the cold pressure of H ₂ 3.0 MPa. The maximum conversion of acetic acid (33.20%) was attained over 0.06MoNi/γ-Al ₂ O ₃ catalysts being reduced at 600 °C under the reaction condition of 200 °C and 3 MPa hydrogen pressure. The hydrogen content in the bio-oil increased from 6.25 wt.% to 6.95 wt.%. The hydrogen content and the acidity, were considerably improved.	Zhang et al. (2010a) Xu et al. (2010a)
Catalytic esterification	Ethanol and bio-oil	A series of solid acids (SO ₄ ²⁻ /ZrO ₂)	The pH value of upgraded bio-oil increased from 2.82 to the highest 7.06, and the gross calorific value increased from 2.82 to the highest 7.06. Moreover, after 3 months of aging, the upgraded bio-oil did not show much viscosity increase.	Xu et al., 2008
Catalyzing esterification	Organic acid Bio-oil	Solid acid (SiO ₂ /TiO ₂ –SO ₄ ²⁻) and solid base (K ₂ CO ₃ /Al ₂ O ₃ –NaOH) catalyst Catalysts of 732- and NKC-9-type ion-exchange resins.	The density of upgraded bio-oil was reduced from 1.24 to 0.96 kg/m ³ , and the acidity of upgraded bio-oil was alleviated by the solid base catalyst.	Zhang et al. (2006)
Esterification	Organic acid in bio-oil	Acidic ionic liquid catalysts	The great mass of organic acids were converted to neutral esters, the heating values increased by 32.26% and 31.64%, and the water contents decreased by 27.74 and 30.87%, respectively. The pH value increased from 2.9 to 5.1, and the water content decreased from 29.8 to 8.2%.	Wang et al. (2010b) Xiong et al. (2009)

(Fitz et al., 2010). Lignocellulose such as woods, straws, and forestry residues, can provide diversified fuels and chemicals as feedstocks and its use is an environmentally conscious alternative to the depleting fossil resources. Catalytic transformation of the constituents of lignocellulose to value added chemicals and fuels has attracted more and more attention because it is presented as an environmentally attractive and energy efficient process compared to the currently used high temperature and energy consuming gasification or pyrolysis technologies (Corma et al., 2007; Huber et al., 2006).

4.1. Cellulose and hemi-cellulose

Cellulose is a linear polymeric structure composed of 41% D-glucose units linked with β-1, 4 glycosidic bonds. It is highly crystalline in nature with the polymeric degree frequently in excess of 9000. Each glucose unit has three hydroxyl groups located on carbon atoms 2, 3, and 6 respectively. The variation in location of these hydroxyl groups confers different chemical activities on the molecule. This allows for the possibility for the various functional modifications on cellulose such as oxidation, esterification, and etherification (Ye and Farriol, 2005). Hydrogen bonds can form between two cellulose units, cellulose and water, and in the interior of cellulose through strong interactions of the hydrogen atoms in hydroxyls and the electronegative oxygen atoms in the other hydroxyls and/or pyrans. The numerous hydrogen bonds present in the cellulose structure confer diverse characteristics on the molecule, such as the ability of self-assembly, crystallinity, inaccessibility, and hygroscopic properties (Ye et al., 2005).

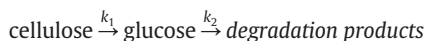
Unlike the uniform assembly of glucose units in cellulose, hemi-cellulose is structurally amorphous and is composed through chemical hybrids of branched heteropolysaccharides (copolymers of any of the monomers of glucose, galactose, mannose, xylose, arabinose,

glucuronic acid, etc.). Hemi-cellulose encompasses cellulose fibers with linkages between the cellulose and lignin. Like cellulose, the hydroxyls in hemi-cellulose macromolecules also take part in a large number of hydrogen bonds. The amorphism of the molecule results in less inaccessibility, and the structure can be easily deconstructed under hydrolysis (Sun et al., 1998).

The use of catalysts is important in the production of potential chemicals and fuels derived from biomass. Cellulose and hemi-cellulose can be catalytically deconstructed to C₆ and C₅ monosaccharides. This process can be followed by further transformation into valuable derivatives through various chemical routes such as hydrolysis, dehydration, hydrogenolysis, hydrogenation, and oxidation (Gallezot, 2010). Research has focused on describing the environment-friendly catalytic processes of important platform molecules and their potential, along with their derivatives, in fine chemical, hydrogen and alkane fuel industries.

4.1.1. Monosaccharides and hexitols

The hydrolytic cleavage of the β-1, 4 glycosidic bonds between two anhydroglucose units (the essential role in cellulose processing) is of fundamental interest as this degradation step can pave the way for subsequent catalytic transformations. However, due to the highly crystalline nature of the structure and the elevated hydrogen bond content, the hydrolysis of cellulose is significantly more challenging than that of starches and hemi-celluloses. Cellulose hydrolysis can be modeled by a pseudo-first-order reaction followed by the transformation of produced glucose to 5-hydroxymethyl furfural (HMF), γ-levalinic acid, formic acid, and lactic acid:



The hydrolysis of cellulose by acid catalysis is generally proposed as a heterogeneous reaction where the catalytic system is in an aqueous

environment and reacts with the insoluble cellulose particles. It is conceivable that the total reaction rate of cellulose degradation is determined by the mass diffusion relative to the crystallization of the cellulosic substrates in micrometer scale dimensions. The mineral acids such as H_2SO_4 , HCl , H_3PO_4 , and HF , organic carboxyl acids such as oxalic, maleic, and fumaric acid, heteropolyacids (HPAs), and cellulose enzymes are used for this degradation (Lee et al., 2009; Salvador et al., 2010; Tian et al., 2010; Xiang et al., 2003). Cellulose degradation with enzymes has obvious drawbacks due to the high costs and long residence times during fermentation. These disadvantages limit their industrialization on a large scale. However, since enzymes generally present high efficiency and mild hydrolytic temperatures, enzymatic hydrolysis of cellulose may become a practicable commercialization approach as further research overcomes the well known cost problem of enzymes. In contrast, hydrolysis by mineral acids and HPAs is inexpensive, fast, and effective. For example, $H_3PW_{12}O_{40}$ as homogeneous catalyst can effectively hydrolyze cellulose to glucose under mild hydrothermal conditions (Tian et al., 2010). Under the optimum conditions (reaction temperature of 180 °C and hydrolyzing duration of 2 h), a glucose yield and selectivity of 50.5% and 90%, respectively, were obtained with trace amounts of levulinic acid and HMF as byproducts. Moreover, the catalyst could be reused at least six times without significant deactivation. This high yield of glucose was attributed to the high hydrothermal stability and strong Brønsted acid sites of HPA.

Although the homogeneous, acidic catalysts demonstrated a high performance in the hydrolysis of cellulose to glucose, the large-scale application of this process for cellulose degradation cannot be commercially implemented due to several disadvantages with the process. The employed homogeneous catalysts generally suffered from energy inefficiency, low catalyst recovery, and equipment corrosion. A thorough separation of products and neutralization of the homogeneous catalyst residues was required producing a large amount of waste. To overcome the aforementioned drawbacks of homogeneous catalysts, much effort has been devoted to using solid acids as heterogeneous catalysts for environmentally conscious processes for cellulose degradation to glucose under mild conditions (Van de et al., 2010b).

The performances of several heterogeneous solid acids for cellulose degradation to glucose are compared in Table 4. Solid acid catalysts, including carbon materials modified by acidification, zeolites, metal oxides and nanocomposites, were usually employed and showed promising catalytic properties in cellulose degradation based on glucose yields. For instance, Onda et al. revealed that sulfonated, activated carbon can convert amorphous ball-milled cellulose to glucose with a yield of 41% and selectivity greater than 90% (Onda et al., 2008). Mesoporous materials have a high surface area and large apertures in the nanometer scale which favor enhanced diffusion rates of the feedstock and products, thereby improving catalytic behavior compared to microporous catalysts. Zhang et al. (2010c) showed that the highest reported glucose yield obtained was 75% by cellulose hydrolysis using sulfonated mesoporous CMK-3 as a catalyst. They also found

that both controlling the sulfonation temperature to obtain strong acidity and selecting a suitable carbon source for better mesopore construction are the key factors in gaining such a high glucose yield. Although heterogeneous catalysts showed high glucose yields in cellulose hydrolysis, there are still several disadvantages that need to be addressed: (1) catalyst stability under harsh, hydrothermal environments (solid catalysts, especially zeolites and some transition metal oxides, undergo structural collapse and chemical transformation); (2) Large quantities of catalyst being used (the high catalyst/cellulose ratio); (3) low cellulose concentration (generally lower than 6 wt.%, which results in low glucose concentration and increases the cost for subsequent transformation. This is due to the condensation of glucose, prior to production of ethanol or other compounds, is energy-consuming), and (4) separation problems of the catalysts from aqueous solution. These disadvantages in cellulose hydrolysis need more intensive investigation in terms of the catalyst composition, crystalline phase, size, and morphology to meet the high stability and efficiency requirements of the solid catalysts. For example, choosing water-tolerant carbon materials as a support was found to be favorable in maintaining a highly stable catalytic performance (Kobayashi et al., 2010). To gain high catalytic efficiency, the solid catalysts are often fabricated into powders with their size in the nanometer scale. This results in a high surface area while making the catalysts difficult to separate from the reaction solution. To overcome this, the use of magnetic catalysts could be applied. The super paramagnetic nanoparticles such as Co, Ni, and Fe_3O_4 could be doped into solid acids to form magnetic nanocomposites which can be easily separated from the reaction system under an external magnetic field (Lai et al., 2010).

Microwaves, as a source of electromagnetic energy, can induce tempestuous oscillation of polar molecules with a frequency of several billions per second and results in the production of heat energy. The inner heating model showed significant accelerating effects by enhancing the reaction rate up to a thousand times over those observed by conventional heating in diversified chemical reactions. Microwave heating is also used to hydrolyze cellulose to its corresponding derivatives (Zhu et al., 2006). For example, Wu et al. (2010b) recently used microwave irradiation to hydrolyze cellulose to glucose in an aqueous phase using sulfonated biomass derived char as a catalyst. This microwave assisted hydrolysis showed a much higher turnover number (TON, 1.33–1.73) compared to the catalysis by dilute H_2SO_4 (TON, 0.02). The difference can be explained by (1) microwave irradiation possibly destructing the crystallinity of cellulose, and (2) microwave irradiation promoting the collision opportunity between solid cellulose and catalyst particles. It was concluded that microwave irradiation also influenced the loss of some of SO_3H groups and decreased glucose yield after recycling the catalyst.

Cellulose is formed by homogeneous glucose units connected via β -1, 4 glycosidic bonds. Large amounts of intermolecular and intramolecular hydrogen bonds contribute to cellulose crystallization and its strong recalcitrance to dissolution or decomposition in water and common solutions. Due to the hydroxyl groups in

Table 4
Hydrolytic degradation of cellulose to glucose with solid acid catalysts (Van de et al., 2010a).

Catalyst	Cellulose type	Substrate concentration ^a (wt.%)	t (h)	T (°C)	Conversion (%)	Yield of glucose (%)
None	Ball-milled	1	24	150	9	<1
Sulfonated activated carbon	Ball-milled	0.9 (1.1)	24	150	43	41
Amorphous carbon bearing SO_3H , $COOH$ and OH	Microcrystalline	3.6 (12)	3	100	100	4 ^b
Silica/carbon nanocomposites	Ball-milled	1 (1)	24	150	61	50
Layered $HNbMoO_6$	Microcrystalline	2 (2)	12	130	n.r. ^c	1
10 wt.% Ru/CMK-3	Ball-milled	0.8 (0.2)	0.25	230	68	34
Sulfonated CMK-3	Ball-milled	1 (1.1)	24	150	94	75

^a Catalysts/substrate ratios shown in parentheses.

^b The main product in this reaction was water-soluble β -1,4-glucan (64% yield).

^c n.r. = not reported.

cellulose construction units, cellulose demonstrates significant affinity to water and other polar solvents and favors further transformation after decomposition. Near- or super-critical water (the critical point: $T_c = 374\text{ }^\circ\text{C}$; $P_c = 22.1\text{ MPa}$; $\rho_c = 323.2\text{ Kg/m}^3$) has a strong solvent capability and showed improved abilities to dissolve cellulose contained in biomass (Malaluan, 1995). Moreover, it's known that liquid water can generate H^+ and OH^- at elevated temperatures (above $200\text{ }^\circ\text{C}$) and is therefore capable of acid/base catalyzed reactions. This in situ formation of acid and base is reversible, and the H^+ and OH^- can disappear automatically as the reaction system is decreased to room temperature, thereby completely eliminating the problems of acid recovery and waste disposal (Luo et al., 2007). Sasaki et al. demonstrated that microcrystalline cellulose could be decomposed into glucose and other derivatives under sub- and super-critical water conditions (25 MPa and $320\text{--}400\text{ }^\circ\text{C}$) (Sasaki et al., 2000). Research on the kinetics of products including cellulose, cellobiose, and glucose showed that at low temperatures (below $350\text{ }^\circ\text{C}$), the cellulose decomposition rate was slower than those of the cellobiose and glucose. At high temperatures ($350\text{--}400\text{ }^\circ\text{C}$), the cellulose decomposition rate drastically increased and became higher than those of cellobiose and glucose, leading to glucose as the main decomposition product. Therefore, the product distribution of cellulose decomposition can be adjusted by changing the temperature of solvent water. In addition to the sub- and supercritical water, ionic liquids also demonstrated good solubilization of cellulose and could convert cellulose to glucose with high yields under mild reaction conditions due to its intrinsic acidity (Ohno and Fukaya, 2009).

Using catalysis with bifunctional metals immobilized on acidic supports, cellulose can be degraded into hexitols by one-pot conversion. Sorbitol is produced by cellulose hydrolysis to glucose over the acidic component of the catalysts followed by hydrogenation over the metal sites. Acidic solid supports such as transition metal oxides, hetero/homo-poly acids and their salts, zeolites, metal-organic frames, acidified resins, metals such as noble Ru, Pt, Pd, transitional Co, Ni and their carbides, and phosphides were combined to obtain a balanced state of metal and acid function of the catalysts. This revealed the synergetic effect for directly converting cellulose to C_6 alcohols (Ding et al., 2010; Palkovits et al., 2010; Yan et al., 2006; Zhu et al., 2010). It was noted that the synergetic effect of bifunctional catalysts is not limited to the solid acids and metals as the soluble mineral acids, hetero/homo-poly acids, and acidic ionic liquids were also found to play an essential role in this transformation (Palkovits et al., 2011; Yan et al., 2006).

4.1.2. Ethylene glycol

Ethylene glycol (EG) as an important fine chemical is widely used in polyester manufacturing and the production of antifreeze. It is mainly synthesized through the hydrolysis of ethylene oxide originating from petroleum, which has implicated its production with environmental and political problems due to the diminishing petroleum resources and the emission of greenhouse gasses. EG has also been indirectly synthesized from coal or biomass-derived syngas by coupling CO and nitrite esters to form oxalates, followed by hydrogenation to EG (Xu et al., 1995; Zhao et al., 2004). However, this multi-step synthetic process has a low efficiency and yield, tedious time constraints and high energy consumption, limiting its industrial application. On the contrary, producing EG by direct decomposition of cellulose via catalytic cracking and hydrogenation in solution shows several economic advantages: (1) the one-pot method avoids the gasification process of biomass to syngas at high temperature and requires less energy as this method is usually conducted at temperatures below $300\text{ }^\circ\text{C}$, and (2) this integrated approach shortens reaction time and improves the production efficiency of EG. Consequently, the direct degradation of cellulose to EG is desirable and has attracted considerable attention.

For this one-pot process, the catalyst choice is critical. Deng et al. prepared Ru catalysts supported on basic $\text{Ca}(\text{OH})_2$ and La_2O_3 , and evaluated their performance in the direct decomposition of cellulose to EG in aqueous phase containing phosphates (H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4). The maximum EG yield was found to be below 20%, demonstrating the limited efficiency of Ru catalysts (Deng et al., 2010). Transition metal phosphides and carbides showed promising catalytic properties in varied chemical reactions due to their platinum-like behaviors (Levy and Boudart, 1973). Zhao et al. (2010a) prepared tungsten phosphide (WP) supported on activated carbon (AC) catalysts, and tested their performance in cellulose degradation to EG. It was found that the use of the WP/AC catalyst resulted in an EG yield of 25%, which could be further increased to 46% as Ni was added. This significant promotion was proposed to be caused by the synergetic effects between Ni and WP components. Moreover, when using Ni promoted W_xC as catalysts, EG yield was increased to 61%, indicating that W_xC has better hydrogenation capabilities compared to WP, thus resulting in a higher EG yield (Ji et al., 2008, 2009). Catalyst supports can significantly alter catalytic properties through strong interactions between the metal and support, and also by promoting diffusion of reactants and products through proper design of pore sizes and dimensions. For example, Zhang et al. (2010c) designed a mesoporous carbon material by the hard template method, and it was used as the support for loading Ni and W_xC particles. The result of cellulose decomposition to EG showed that the yield further increased to 74%. This is due to the significant diffusion enhancement of cellulose and products through the mesoporous carbon pores suppressing the formation of byproducts.

4.1.3. 5-Hydroxymethyl furfural

Production of value-added intermediates through chemical transformation of sustainable biomass by catalysis is a promising substitute for the irreversible chemicals produced from fossil resources. Through the downstream conversion of these intermediate or platform molecules, biomass can produce prolific chemicals and materials which are comparable to those produced from fossil fuel resources. The chemical, 5-Hydroxymethyl furfural (HMF), which is the dehydration product of hexoses, is one such of these platform molecules. HMF can further be converted to versatile downstream products including levulinic acid, 2, 5-dimethyl furan, 2, 5-furan dicarboxylic acid, 2, 5-dihydroxymethyl furan, other furan and tetrahydrofuran derivatives, and alkanes. Methods of conversion include fractionation of gasoline and diesel by catalytic oxidation, hydrogenation, hydrodeoxygenation, and C–C bond coupling of HMF with small molecular ketone and aldehyde compounds. These HMF derived products have potential applications in fine chemical and polymeric industries since their chemical groups are easily converted. Therefore, advances in HMF production will be of great significance for the transformation of biomass into bio-based chemicals and biofuels (Gallezot, 2007; Tong et al., 2010).

Versatile acids, including mineral acids (HCl , H_2SO_4 , H_3PO_4), organic acids (oxalic acid, formic acid), and solid acids (metal oxides, zeolites, acidic resins), were used for the synthesis of HMF in different solutions including water, organic solvent, organic/water mixtures, and supercritical solvents. The renewable starting materials used were diversified biomass such as glucose, fructose, sucrose, cellobiose, cellulose, and starch (Asghari and Yoshida, 2006; Chheda et al., 2007; Kuster, 1990). The use of mineral acids showed effective production of HMF from fructose and glucose, but due to their notorious corrosion of the reactor and the liquid waste that was discharged, the mineral acid catalyzed processes were limited. Solid acids and supercritical water are environmentally friendly catalysts for synthesizing HMF because they can be easily recovered from reaction systems and can drastically reduce waste discharge, but their catalytic efficiencies (the low HMF yield) are not satisfactory (Zhang et al., 2010e). Supercritical water showed similar properties to solid acids

and could also be used as a catalyst for the synthesis of HMF, but a low HMF yield was obtained (below 40%) possibly due to its weak acidity (Qi et al., 2008). Ionic liquids as green solvents and acidic catalysts are widely used in various chemical synthesis reactions including HMF production from biomass. Owing to the unique reaction environment that ionic liquids present, HMF yields can reach more than 90% when using fructose as the feedstock (Li et al., 2010a). On the other hand, microwave promotion and integrated enzymatic and acid catalysis were the other alternatives in HMF production that could obtain significantly increased HMF yields even when using glucose and polysaccharides as the feedstocks (Huang et al., 2010; Li et al., 2009a; Qi et al., 2008).

The yield of HMF is influenced by biomass sources due to the structural discrepancy between C₆ ketose and aldose units. Reaction mechanistic studies demonstrated that HMF formation by aldose dehydration is produced by two sequential steps: (1) isomerization of aldose to the corresponding ketose, and (2) conversion of the ketose dehydrates to HMF. Since isomerization of the aldose is proposed as the rate determined step, HMF from ketose dehydration is favorable and can obtain significantly higher HMF yields compared to aldoses. Although aldoses such as glucose are not easily converted to HMF, they have lower cost and higher abundance than fructose. It is therefore significant to obtain high yields of HMF by glucose dehydration. Recently, a breakthrough has been made to achieve high HMF yields of greater than 90% in coupling systems containing metal chlorides such as CrCl₂ and GeCl₄, and ionic liquids (Zhang et al., 2010d; Zhao et al., 2007b). The high HMF yields obtained were credited to the combination of metal chlorides and ionic liquids as unique ligands for accelerating the mutarotation and isomerization of glucose to fructose. This resulted in a significant increase in the apparent dehydration rate of glucose to form HMF.

4.1.4. Biofuels

Since the 1950s, highly efficient refining technologies based on petroleum feedstocks have been developed for obtaining the wide range of carbon chain lengths in fossil fuels such as hydrogen, natural gas, liquefied petroleum gas, little naphtha, gasoline, kerosene, and diesel. Biomass is abundant, easily available, and renewable, and can produce versatile fuels to support human development. However, because of the high oxygen content in biomass resources, the processes which are effective for petroleum are not suitable for biomass. Considering the low thermal stability and highly functionality (for example the intrinsic hydrophilicity) of biomass molecules, a biorefinery method of converting biomass to biofuels containing hydrogen and alkanes was implemented under the particular conditions of aqueous-phase reforming (APR) (Huber et al., 2004).

4.1.4.1. H₂ production. Hydrogen is a clean fuel with the following advantages: no waste formation because water is the only product during hydrogen combustion, and a high energy density (the formation enthalpy of water (ΔH_f) is 285.83 kJ/mol). Highly efficient and sustainable H₂ production by APR of carbohydrates demonstrated significant advantages: (1) APR reactions occur in liquid water, and the gasification of water and carbohydrates is avoided, greatly reducing the energy consumption, (2) carbohydrates are nontoxic and nonflammable and are stored and processed, (3) the water–gas shift reaction that can occur at the temperature and pressure conditions of APR significantly decreases the CO content in the products, (4) the CO₂ produced can be easily separated from the reaction system by pressure swing adsorption at the APR pressure of 15–50 bar, and (5) APR occurs at low temperatures (below 260 °C), which greatly suppresses the formation of byproducts produced by the decomposition and carbonization of biomass feedstocks. Therefore, H₂ production via APR of biomass is of scientific significance and has captured worldwide attention (Cortright et al., 2002).

The catalyst plays an essential role in H₂ production by APR of carbohydrates and their oxygenated derivatives including monosaccharides and polyols (sorbitol, mannitol, xylitol, glycerol and ethylene glycol). The H₂ yield can be significantly improved by the proper choice of catalyst metals, supports, and assembly. For example, supported Pt showed high H₂ selectivity in APR of ethylene glycol (Cortright et al., 2002). The non-precious metal Ni was also used for this reaction but suffered from fast deactivation and high methane content due to carbon deposition and the methanation of CO and CO₂. Over an NiSn catalyst, the rate of methanation from C–O cleavages greatly decreased while keeping a high rate of C–C cracking. A high H₂ yield comparable to that achieved with Pt was obtained (Huber et al., 2003). Wen et al. compared the effects of catalyst supports in biomass-derived glycerol over Pt catalysts, and found that a basic support such as MgO is favorable to get high H₂ selectivity. It was also determined that while on the acidic supports such as USY and SAPO-11, the catalysts suffered fast deactivation due to carbon deposition (Wen et al., 2008). Biomass feedstocks significantly influenced H₂ yields in APR reactions. Wen et al. demonstrated that the H₂ yields increased in the following order of substrates: fructose < glucose < sorbitol < glycerol < ethylene glycol. Hydrocarbon selectivities presented the opposite sequence (Wen et al., 2009). The low H₂ yields obtained by the polyols and monosaccharides with long carbon chains is perhaps due to the fact that these compounds encounter side reactions such as condensation, decomposition, and hydrogenation. Cellulose can be directly transferred into H₂ by the APR approach over Pt/C catalysts, but the H₂ yield is low due to its microcrystallinity which is resistant to decomposition under APR reaction conditions (Wen et al., 2010). Due to CO₂ in effluent products, H₂ yield is limited by thermodynamic equilibrium. To break this equilibrium, bases such as KOH and NaOH can be introduced into the APR reaction system and act as the stoichiometric agents to combine with the product CO₂ to form K₂CO₃ and Na₂CO₃. This promoted the reaction to shift right and achieve a very high H₂ yield of greater than 90% (Liu et al., 2010).

4.1.4.2. Liquid alkanes. Compared to the combustion of the liquid alkane fuels originating from refining fossil resources, utilization of biomass-derived liquid alkanes as transportation fuels can greatly decrease negative environmental impacts. Biomass-derived alkanes in the distillation range of the gasoline fraction can be produced by dehydration and hydrogenation of C₅ and C₆ sugars or the relative polyols over metal supported solid acids catalysts (Huber et al., 2004).

The caloric values of the energy efficiency in alkanes produced by APR were compared with glucose and n-hexane. Glucose and H₂ combustion releases an enthalpy of 2600 kJ/mol and 1700 kJ/mol, respectively, while n-hexane produced by hydrogenation of glucose liberates an enthalpy of 3900 kJ/mol (Dean, 1999). Hydrogenation of carbohydrates to alkanes requires large amounts of H₂, since every mol of C atoms in carbohydrates requires 1 mol of H₂. An obvious advantage of liquid alkanes synthesized by APR of biomass is that the alkanes can automatically separate from the aqueous phase due to their hydrophobicity, thereby avoiding the energy consuming distillation process commonly used for producing alkanes from fossil resources.

Bifunctional catalysts of metal (Pt, Pd, Ni, Co) supported by solid acids (metal oxides, SiO₂–Al₂O₃, zeolites) were used for converting C₅ and C₆ sugars, and the corresponding polyols and derivatives into liquid alkanes. For example, Zhang et al. (2010b) reported that Ni supported SiO₂–Al₂O₃ catalysts could effectively convert a furfural platform compound (a derivative of xylose) to pentanes with a high yield. Generally, APR of biomass-derived sugars and polyols to liquid alkanes is a multi-step reaction. Taking sorbitol as an example, the first step of the reaction is the dehydration to form cyclic (isosorbide) or enol intermediates by the acidic function of the catalyst. These intermediates are then shifted to metal sites for hydrogenation to form

alkanes (Kunke et al., 2008; West et al., 2009). Alkane selectivity in APR is the result of synergetic C–C cleavages, dehydration, and hydrogenation. Controlling the composition of the catalysts and the interaction between metals and supports to achieve the appropriate acid (dehydration) and metal (hydrogenation) balance is of significant importance.

In the case of biogasoline production from biomass APR at a medium scale, experts of GIEC/CAS built a demonstration process in Yingkou, Liaoning province, China. This demonstration process could produce C₅ and C₆ alkanes with the scale of 150 ton/a by using the sugar-contained hydrolysis liquor as feedstock. The success of this process could play a substantial role in forcing the development of biogasoline in China.

4.2. Lignin

Lignin is one of the three major components of lignocellulose biomass along with cellulose and hemicellulose. In plant cells, lignin fills the spaces between cellulose and hemicellulose and acts as a resin to strengthen the lignocellulose matrix. Every year, millions of tons of lignin as black liquor are produced by the paper industry. To favor the comprehensive profits and counteract the negative environmental impact, most of these black liquor byproducts are burned to recover inorganic additives for recycling to the pulping processes, while also generating energy for the pulp mill. Lignin is comprised of three primary phenol-contained components: p-hydroxyphenyl, guaiacol, and syringyl units which are linked with C–O (β -O-4, α -O-4, and 4-O-5 linking style) and C–C (β -5, 5-5, β -1, β - β linking style) bonds (Calvo-Flores and Dobado, 2010). As an important renewable biomass resource, lignin macromolecules contain versatile chemical groups of phenyl, double carbon–carbon bonds, ethers, hydroxyls, carbonyls, and carboxyls. This variety of chemical groups makes lignin highly desirable for the production of various chemicals and biofuels through diverse chemical modifications: catalytic degradation, alkylation, oxidation, and hydrogenation, to name a few (Zakzeski et al., 2010). Compared to cellulose and hemicellulose, however, catalytic transformation of lignin to chemicals and fuels is less explored possibly due to its structural complexity and recalcitrance to decomposition.

4.2.1. Vanillin

Vanillin is the main component of natural vanilla extract and is widely used as a flavoring agent in food, fragrances, beverages, and pharmaceuticals. The market demand for vanillin has far exceeded the supply of vanilla beans. Consequently, synthetic methods have been developed for many years. The first synthesis of vanillin was performed using eugenol (which is originated from clover oil) as starting material, but currently, it is predominantly and economically produced from lignin sulfonates. Since 1993, the Norwegian company Borreagaard has been the sole vanillin producer. Borreagaard's process is economically feasible and can be described as environmentally friendly since the CO₂ emissions have been proven to be 90% lower than those resulting from vanillin from the petrochemical industry.

4.2.2. Aromatics and derivatives

Due to the ubiquitous phenyl groups in the p-hydroxyphenyl, guaiacol, and syringyl units in lignin, it is desirable to produce chemicals containing aromatics and their derivatives from lignin by catalytic processes. For example, Zhao et al. (2010b) developed a promising method to produce aromatics from lignin derived from catalytic pyrolysis. In the presence of HZSM-5, the aromatics yield (carbon yield) was as high as 39% with a phenol selectivity of 87%, demonstrating an alternative route for the sustainable production of aromatics from biomass resources. Moreover, if using oxidative catalysts (for example, the perovskite-type oxide LaCoO₃), the aldehyde-containing derivatives such as p-hydroxybenzaldehyde,

vanillin, and syringaldehyde could be obtained from lignin with high yields (Deng et al., 2009).

4.2.3. Carbon materials

Activated carbon can be produced from lignin with a process involving two sequential steps (Guo and Rockstraw, 2006). At the first stage, lignin is pyrolytically carbonized to char in the temperature range of 600–850 °C. In this process, a nonporous material is obtained that must be activated. Activation of the produced char, with the aim of making it microporous, is the second stage. This activation can be achieved by the physical method of treating the char with an oxidant gas such as steam or CO₂ in a temperature range of 600–850 °C. Another option is the chemical method of impregnating char with H₃PO₄, KOH, or NaOH used as catalysts followed by heating under a nitrogen flow at 450–850 °C.

4.2.4. Biofuels

Another approach for converting lignin into valuable products is to synthesize renewable liquid alkane fuels. This process can reduce pollution and CO₂ emissions and can also improve the economic benefits for pulp and paper manufacturers. This conversion can be accomplished by hydrolysis, dehydration, hydrogenation, and hydrogenolysis over supported metal catalysts in water, organic, or mixed solutions (Zhao et al., 2009).

Lignin is a complex macromolecule constructed by phenylpropane units linked by C–C and C–O–C bonds. For producing liquid alkanes from lignin by hydrogenolysis, two sequential steps are involved. Firstly, the C–O–C linkages among lignins are split under H₂ attack to form the monomers and dimers of the phenylpropane building block. Secondly, the unsaturated groups including phenyl, C=C bond, and hydroxyls in the monomers and dimers are further hydrogenated and hydrodeoxygenated to the saturated alkanes with the carbon number distribution in range of gasoline and diesel. Due to the structural stubbornness of lignin, alkanes were usually produced under high temperatures and pressures with the presence of catalysts (the metals such as Pt, Pd, Rh, Ru immobilized on water-tolerant supports). For example, Kou et al. prepared Pt, Pd, and Rh supported carbon catalysts for producing alkanes from birch lignin. The reaction conditions were 250 °C, 4 MPa (H₂ pressure), and 2 h in an aqueous solution of 5% H₃PO₄. The obtained yield was 42 wt.% C₈–C₉ and 10 wt.% C₁₄–C₁₈ alkanes with about 11 wt.% of methanol as a byproduct (Yan et al., 2008). Furthermore, by using colloidal Rh and Pt stabilized by acidic ionic liquids as nanocatalysts, the alkane yields can be significantly improved (Yan et al., 2010; Zhao et al., 2007a).

5. Status and prospect

R&D on first- and second-generation biofuel technologies and processes has been carried out in China. First-generation biofuels include ethanol and butanol, produced by the hydrolysis or fermentation of starches or sugar, and biodiesel, produced by the transesterification of plant oil. Limitations of first-generation biofuels include direct competition between using feedstocks for food and fuel production and the utilization of only a portion of the total biomass. China had banned the development of corn-to-ethanol processes. Furthermore, due to limitations in plant oil resources, the commercialization of biodiesel is challenging.

The development of second-generation biofuels is promising due to their use of a non-edible feedstock, lignocellulosic biomass, which is composed of either crop residuals (corn stalks or rice husks), woody crops, or energy grasses. Bio- and thermal–chemical processes have been developed using enzymatic hydrolysis to produce ethanol or butanol and by gasification/synthesis to produce methanol, dimethyl ether (DME), mixed alcohols, and FT gasoline/diesel. Currently, enzymatic hydrolysis of lignocellulosic biomass is costly and the energy consumption of distilling ethanol or butanol from water is high.

Thermal-chemical processes have gained attention since 2005. Biomass gasification and combustion technologies are employed widely in China. Future work should focus on the standard of the unit, automatic operation, and increasing efficiency. The technology of bio-oil production was developed in China over 20 years, but raw bio-oil upgrading technologies have not made great progress. Currently, bio-oil is only used for combustion in boilers, and additional research is required to improve the quality of bio-oil for other applications. Catalytic transformation of biomass is a promising technology for the conversion of biomass into valuable products and has gained significant attention by the Chinese government.

Considering the inherent disadvantages of these respective conversion approaches for non-edible lignocellulosic biomass, coupling multiple technologies will enable the conversion of lignocellulosic biomass with higher energy efficiency and comprehensive profit. While biomass gasification shows relatively low energy efficiency and yields gasses having low heating values, improvements could be achieved by tailoring towards the syngas component followed by catalytic F-T synthesis to produce hydrocarbons, DME, and mixed alcohols with low carbon numbers for clean and advanced fuel applications. Generally, cellulose and hemi-cellulose could be completely degraded by hydrolysis with lignin as the residues. The coupling of hydrolysis and gasification/liquefaction with the aim to convert lignin that is hardly decomposed by hydrolysis could achieve complete transformation of lignocellulosic biomass.

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References

- Asghari FS, Yoshida H. Dehydration of fructose to 5-hydroxymethylfurfural in subcritical water over heterogeneous zirconium phosphate catalysts. *Carbohydr Res* 2006;341:2379–87.
- Bridgewater AV, Peacocke GVC. Fast pyrolysis processes for biomass. *Renewable Sustainable Energy Rev* 2000;4:1–73.
- Bunch AY, Wang XQ, Ozkan US. Adsorption characteristics of reduced Mo and Ni–Mo catalysts in the hydrodeoxygenation of benzofuran. *Appl Catal, A* 2008;346(1–2, 31):96–103.
- Calvo-Flores FG, Dobado JA. Lignin as renewable raw material. *ChemSusChem* 2010;3:1227–35.
- Chen MQ, Wang J, Zhang MX, Chen MG, Zhu XF, Min FF, et al. Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating. *J Anal Appl Pyrolysis* 2008;82:145–50.
- Chen Y, Wang C, Lu W, Yang Z. Study of the co-deoxy-liquefaction of biomass and vegetable oil for hydrocarbon oil production. *Bioresour Technol* 2010;101:4600–7.
- Chheda JN, Roman-Leshkov Y, Dumesic JA. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem* 2007;9:342–50.
- Corma A, Iborra S, Velty A. Chemical routes for the transformation of biomass into chemicals. *Chem Rev* 2007;107:2411–502.
- Cortright RD, Davda RR, Dumesic JA. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 2002;418:964–7.
- Dai X, Wu C, Li H, Chen Y. The fast pyrolysis of biomass in CFB reactor. *Energy Fuel* 2000;14:552–7.
- Dean JA. *Lange's handbook of chemistry*. New York: McGraw-Hill; 1999.
- Demirbas A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Convers Manage* 2008;49:2106–16.
- Deng HB, Lin L, Sun Y, Pang CS, Zhuang JP, Ouyang PK, et al. Activity and stability of perovskite-type oxide LaCoO₃ catalyst in lignin catalytic wet oxidation to aromatic aldehydes process. *Energy Fuels* 2009;23:19–24.
- Deng TY, Sun JY, Liu HC. Cellulose conversion to polyols on supported Ru catalysts. *Sci Chin Chem* 2010;53:1476–80.
- Ding LN, Wang AQ, Zheng MY, Zhang T. Selective transformation of cellulose into sorbitol by using a bifunctional nickel phosphide catalyst. *ChemSusChem* 2010;3:818–21.
- El harfi K, Mokhlisse A, Chan A MB, Outzourhit A. Pyrolysis of the Moroccan (Tarfaya) oil shales under microwave irradiation. *Fuel* 2000;79:733–42.
- Fitz PM, Champagne P, Cunningham MF, Whitney RA. A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. *Bioresour Technol* 2010;101:8915–22.
- Gallezot P. Catalytic routes from renewables to fine chemicals. *Catal Today* 2007;121:76–91.
- Gallezot P. Alternative value chains for biomass conversion to chemicals. *Top Catal* 2010;53:1209–13.
- Guo YP, Rockstraw DA. Physical and chemical properties of carbons synthesized from xylan, cellulose, and Kraft lignin by H₃PO₄ activation. *Carbon* 2006;44:1464–75.
- Hamelinck CN, Faaij APC. Outlook for advanced biofuels. *Energy Policy* 2006;34:32–68.
- Hao XH, Guo LJ, Mao X, Zhang XM, Chen XJ. Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water. *Int J Hydrogen Energy* 2003;28:55–64.
- Huang RL, Qi W, Su RX, He ZM. Integrating enzymatic and acid catalysis to convert glucose into 5-hydroxymethylfurfural. *Chem Commun* 2010;46:1115–7.
- Huang H, Yuan X, Zeng G, Wang J, Li H, Zhou C, et al. Thermochemical liquefaction characteristics of microalgae in sub- and supercritical ethanol. *Fuel Process Technol* 2011;92:147–53.
- Huber GW, Shabaker JW, Dumesic JA. Raney Ni–Sn catalyst for H₂ production from biomass-derived hydrocarbons. *Science* 2003;300:2075–7.
- Huber GW, Cortright RD, Dumesic JA. Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angew Chem Int Ed* 2004;43:1549–51.
- Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem Rev* 2006;106:4044–98.
- Ikura M, Stanculescu M, Hogan E. Emulsification of pyrolysis derived bio-oil in diesel fuel. *Biomass Bioenergy* 2003;24:221–32.
- Ji N, Zhang T, Zheng MY, Wang AQ, Wang H, Wang XD, et al. Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts. *Angew Chem Int Ed* 2008;47:8510–3.
- Ji N, Zhang T, Zheng MY, Wang AQ, Wang H, Wang XD, et al. Catalytic conversion of cellulose into ethylene glycol over supported carbide catalysts. *Catal Today* 2009;147:77–85.
- Jung SH, Kang BS, Kim JS. Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. *J Anal Appl Pyrolysis* 2008;82:240–7.
- Kobayashi H, Komanoya T, Hara K, Fukuoka A. Water-tolerant mesoporous-carbon-supported ruthenium catalysts for the hydrolysis of cellulose to glucose. *ChemSusChem* 2010;3:440–3.
- Kunkes EL, Simonetti DA, West RM. Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes. *Science* 2008;322:417–21.
- Kuster BFM. 5-hydroxymethyl furfural (HMF)—a review focusing its manufacture. *Starch* 1990;42:314–21.
- Lai DM, Deng L, Li J, Liao B, Guo QX, Fu Y. Hydrolysis of cellulose into glucose by magnetic solid acid. *ChemSusChem* 2010:1–4.
- Lee JW, Rodrigues RCLB, Jeffries TW. Simultaneous saccharification and ethanol fermentation of oxalic acid pretreated corncob assessed with response surface methodology. *Bioresour Technol* 2009;100:6307–11.
- Leung YCD, Yin X, Wu C. A review on the development and commercialization of biomass gasification technologies in China. *Renewable Sustainable Energy Rev* 2004;8:565–80.
- Levy RB, Boudart M. Platinum-like Behavior of tungsten carbide in surface catalysis. *Science* 1973;181:547–9.
- Li J, Wu L, Yang Z. Analysis and upgrading of bio-petroleum from biomass by direct deoxy-liquefaction. *J Anal Appl Pyrolysis* 2008;81:199–204.
- Li CZ, Zhang ZH, Zhao ZBK. Direct conversion of glucose and cellulose to 5-hydroxymethylfurfural in ionic liquid under microwave irradiation. *Tetrahedron Lett* 2009a;50:5403–5.
- Li H, Shen B, Kabalu JC, Nchare M. Enhancing the production of biofuels from cottonseed oil by fixed-fluidized bed catalytic cracking. *Renewable Energy* 2009b;34:1033–9.
- Li H, Yuan X, Zeng G, Tong J, Yan Y, Cao H, et al. Liquefaction of rice straw in sub- and supercritical 1,4-dioxane–water mixture. *Fuel Process Technol* 2009c;90:657–63.
- Li Y, Wang T, Yin X, Wu C, Ma L, Li H, et al. Design and operation of integrated pilot-scale dimethyl ether synthesis system via pyrolysis/gasification of corncob. *Fuel* 2009d;88:2181–7.
- Li CZ, Zhao ZBK, Wang AQ, Zheng MY, Zhang T. Production of 5-hydroxymethylfurfural in ionic liquids under high fructose concentration conditions. *Carbohydr Res* 2010a;345:1846–50.
- Li Y, Wang T, Yin X, Wu C, Ma L, Li H, et al. 100 t/a-Scale demonstration of direct dimethyl ether synthesis from corncob-derived syngas. *Renewable Energy* 2010b;35(3):583–7.
- Liu ZG, Zhang FS. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Convers Manage* 2008;49:3498–504.
- Liu R, Lu N, Cao Y. Technological process and experimental research of the rotating cone reactor for biomass pyrolysis. *J Shenyang Agric Univ* 1997;28:307–11.
- Liu CY, Lu Q, Sun SS, Zhang D, Zhu XF. Research on rice husk bio-oil combustion and pollutant emissions. *J Fuel Chem Technol* 2008;36(5):577–82. (in Chinese).
- Liu J, Chu XW, Zhu LJ, Hu JY, Dai R, Xie SH, et al. Simultaneous aqueous-phase reforming and KOH carbonation to produce CO_x-free hydrogen in a single reactor. *ChemSusChem* 2010;3:803–6.
- LoÃ pez Juste G, SalvaÃ MJJ. Preliminary test on combustion of wood derived fast pyrolysis oils in a gas turbine combustor. *Biomass Bioenergy* 2000;19:119–28.

- Lu C, Yao J, Lin W, Song W. Study on biomass catalytic pyrolysis for production of bio-gasoline by on-line FTIR. *Chin Chem Lett* 2007;18:445–8.
- Lu YJ, Jin H, Guo LJ, Zhang XM, Cao CQ, Guo X. Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor. *Int J Hydrogen Energy* 2008;33:6066–75.
- Lu W, Wang C, Yang Z. The preparation of high calorific fuel (HCF) from water hyacinth by deoxy-liquefaction. *Bioresour Technol* 2009;100:6451–6.
- Luo C, Wang S, Liu HC. Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water. *Angew Chem Int Ed* 2007;46:7636–9.
- Lv Y, Wang T, Wu C, Ma L, Zhou Y. Scale study of direct synthesis of dimethyl ether from biomass synthesis gas. *Biotechnol Adv* 2009;27(5):551–4.
- Malaluan RM. A Study on cellulose decomposition in subcritical and supercritical water. Ph.D. Dissertation, Tohoku University, Sendai, Japan, 1995.
- Martinez AT, Speranza M, Ruiz-Duenas FJ, Ferreira P, Camarero S, Guillen F, et al. Biodegradation of lignocelluloses: microbial chemical, and enzymatic aspects of the fungal attack of lignin. *Int Microbiol* 2005;8:195–204.
- Ohno H, Fukaya Y. Task specific ionic liquids for cellulose technology. *Chem Lett* 2009;38:2–7.
- Onda A, Ochi T, Yanagisawa K. Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem* 2008;10:1033–7.
- Palkovits R, Tajvidi K, Procelewska J, Rinaldi R, Ruppert A. Hydrogenolysis of cellulose combining mineral acids and hydrogenation catalysts. *Green Chem* 2010;12:972–8.
- Palkovits R, Tajvidi K, Ruppert AM, Procelewska J. Heteropoly acids as efficient acid catalysts in the one-step conversion of cellulose to sugar alcohols. *Chem Commun* 2011;47:576–8.
- Peng J, Chen P, Lou H, Zheng XM. Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol. *Bioresour Technol* 2009;100:3415–8.
- Peng J, Fan Z, Chen G. Progress in upgrading or refinery of bio-oil. *Chem Ind Eng Prog* 2010;29(6):1034–40. (in Chinese).
- People's Congress. The Law of People's Republic of China Renewable Energy; 2005.
- Qi XH, Watanabe M, Aida TM, Smith Jr RL. Catalytic conversion of fructose and glucose into 5-hydroxymethylfurfural in hot compressed water by microwave heating. *Catal Commun* 2008;9:2244–9.
- Roy C, Chhala A. Vacuum pyrolysis of automobile shredder residues. *Resour Conserv Recycl* 2001;32:1–27.
- Salvador AC, Santos MD, Saraiva JA. Effect of the ionic liquid [bmim]Cl and high pressure on the activity of cellulose. *Green Chem* 2010;12:632–5.
- Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K. Dissolution and hydrolysis of cellulose in subcritical and supercritical water. *Ind Eng Chem Res* 2000;39:2883–90.
- Shao Q, Peng J, Xiu S, Wen X. Analysis of oil products by pyrolysis of bamboo in supercritical methanol. *Acta Energiae Solaris Sin* 2007;28:984–7.
- Sun RC, Mark LJ, Banks WB. Isolation and characterization of hemicellulose B and cellulose from pressure refined wheat straw. *Ind Crops Prod* 1998;7:121–8.
- Sun P, Heng M, Sun S, Chen J. Direct liquefaction of paulownia in hot compressed water: influence of catalysts. *Energy* 2010;35:5421–9.
- Sun B, Liu Y, Chen X, Zhou Q, Su M. Dynamic modeling and simulation of shell gasifier in IGCC. *Fuel Process Technol* 2011a;92:1418–25.
- Sun P, Heng M, Sun S, Chen J. Analysis of liquid and solid products from liquefaction of paulownia in hot-compressed water. *Energy Convers Manage* 2011b;52:924–33.
- Tan J, Sun SS, Zhu XF. Research progress of bio-oil application technology in diesel engine. *Biomass Chem Eng* 2008;42(5):43–5. (in Chinese).
- Tian J, Wang JH, Zhao S, Jiang CY, Zhang X, Wang XH. Hydrolysis of cellulose by the heteropoly acid H₃PW₁₂O₄₀. *Cellulose* 2010;17:587–94.
- Tong XL, Ma Y, Li YD. Biomass into chemicals: conversion of sugars to furan derivatives by catalytic processes. *Appl Catal*. A 2010;385:1–13.
- Van de VS, D'Hondt E, Sels BF, Jacobs PA. Preparation of Pt on NaY zeolite catalysts for conversion of glycerol into 1,2-propanediol. *Stud Surf Sci Catal* 2010a;175:771–4.
- Van de VS, Geboers J, Jacobs PA, Sels BF. Recent advances in the catalytic conversion of cellulose. *ChemCatChem* 2010b. doi:10.1002/cctc.201000302.
- Wan Y, Chen P, Zhang B, Yang C, Liu Y, Lin X, et al. Microwave-assisted pyrolysis of biomass: catalysts to improve product selectivity. *J Anal Appl Pyrolysis* 2009;86:161–7.
- Wang S, Fang M, Yu C, Luo Z, Cen K. Flash pyrolysis of biomass particles in fluidized bed for bio-oil production. *Chin Particuol* 2005;3:136–40.
- Wang T, Chang J, Cui X, Zhang Q, Fu Y. Reforming of raw fuel gas from biomass gasification to syngas over highly stable nickel–magnesium solid solution catalysts. *Fuel Process Technol* 2006;87:421–8.
- Wang G, Li W, Li B, Chen H, Bai J. Direct liquefaction of sawdust under syngas with and without catalyst. *Chem Eng Process* 2007a;46:187–92.
- Wang G, Li W, Li B, Chen H. Direct liquefaction of sawdust under syngas. *Fuel* 2007b;158:7–93.
- Wang C, Pan J, Li J, Yang Z. Comparative studies of products produced from four different biomass samples via deoxy-liquefaction. *Bioresour Technol* 2008;99:2778–86.
- Wang W, Yang Y, Luo H, Liu W. Effect of additive (Co, La) for Ni–Mo–B amorphous catalyst and its hydrodeoxygenation properties. *Catal Commun* 2010a;11:803–7.
- Wang J, Chang J, Fan J. Catalytic esterification of bio-oil by ion exchange resins. *J Fuel Chem Technol* 2010b;38:560–4.
- Wen GD, Xu YP, Ma HJ, Xu ZS, Tian ZJ. Production of hydrogen by aqueous-phase reforming of glycerol. *Int J Hydrogen Energy* 2008;33:6657–66.
- Wen GD, Xu YP, Wei Y, Pei RY, Li KD, Xu ZS, et al. Hydrogen production by aqueous-phase reforming of biomass over supported Pt catalysts. *Chin J Catal* 2009;30:830–5.
- Wen GD, Xu YP, Xu ZS, Tian ZJ. Direct conversion of cellulose into hydrogen by aqueous-phase reforming process. *Catal Commun* 2010;11:522–6.
- West RM, Tucker MH, Braden DJ. Production of alkanes from biomass derived carbohydrates on bifunctional catalysts employing niobium-based supports. *Catal Commun* 2009;10:1743–6.
- Wu C, Huang H, Zheng SP, Yin XL. An economic analysis of biomass gasification and power generation in China. *Bioresour Technol* 2002;83(1):65–70.
- Wu C, Huang Q, Sui M, Yan Y, Wang F. Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system. *Fuel Process Technol* 2008;89:1306–16.
- Wu L, Guo S, Wang C, Yang Z. Production of alkanes (C7–C29) from different part of poplar tree via direct deoxy-liquefaction. *Bioresour Technol* 2009a;100:2069–76.
- Wu C, Yin X, Ma L, Zhou Z, Chen H. Operational characteristics of a 1.2-MW biomass gasification and power generation plant. *Biotechnol Adv* 2009b;27(5):588–92.
- Wu CZ, Yin XL, Yuan ZH, Zhou ZQ, Zhuang XS. The development of bioenergy technology in China. *Energy* 2010a;35:4445–50.
- Wu YY, Fu ZH, Yin DL, Xu Q, Liu FL, Lu CL, et al. Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids. *Green Chem* 2010b;12:696–700.
- Xiang Q, Lee YY, Pettersson PO, Torget R. Heterogeneous aspects of acid hydrolysis of alpha-cellulose. *Appl Biochem Biotechnol* 2003;105:505–14.
- Xie W, Yuan XZ, Zeng GM, Tong JY, Li H. Effects of catalysts on biomass liquefaction in subcritical water. *Resour Sci (Chinese)* 2008;30:129–33.
- Xiong WM, Zhu MZ, Deng L, Fu Y, Guo QX. Esterification of organic acid in bio-oil using acidic ionic liquid catalysts. *Energy Fuels* 2009;23(4):2278–83.
- Xu C, Etcheverry T. Hydro-liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts. *Fuel* 2008;87:335–45.
- Xu GH, Li YC, Li ZH, Wang HJ. Kinetics of the hydrogenation of diethyl oxalate to ethylene glycol. *Ind Eng Chem Res* 1995;34:2371–8.
- Xu BJ, Li ML, Zeng Z, Lu M. The system of the rotating cone pyrolysis for biomass and the dynamics of heat carrier. *J. Univ Shanghai Science Technol* 2000;22:16–20.
- Xu J, Jiang J, Sun Y, Lu Y. A novel method of upgrading bio-oil by reactive rectification. *J Fuel Chem Technol* 2008;36:421–5.
- Xu Y, Wang T, Ma L, Zhang Q, Wang L. Upgrading of liquid fuel from the vacuum pyrolysis of biomass over the Mo–Ni/γ-Al₂O₃ catalysts. *Biomass Bioenergy* 2009;33:1030–6.
- Xu Y, Wang TJ, Ma LL, Zhang Q, Liang W. Upgrading of the liquid fuel from fast pyrolysis of biomass over MoNi/γ-Al₂O₃ catalysts. *Appl Energy* 2010a;87:2886–91.
- Xu YF, Wang QJ, Hua XG, Li C, Zhu XF. Characterization of the lubricity of bio-oil/diesel fuel blends by high frequency reciprocating test rig. *Energy* 2010b;35:283–7.
- Yan N, Zhao C, Luo C, Dyson PJ, Liu HC, Kou Y. One-step conversion of cellulose to C6-alcohols using a ruthenium nanocluster catalyst. *J Am Chem Soc* 2006;128:8714–5.
- Yan N, Zhao C, Dyson PJ, Wang C, Liu LT, Kou Y. Selective degradation of wood lignin over noble-metal catalysts in a two-step process. *ChemSusChem* 2008;1:626–9.
- Yan N, Yuan Y, Dykeman R, Kou Y, Dyson PJ. Hydrodeoxygenation of lignin-derived phenols into alkanes by using nanoparticle catalysts combined with Brønsted acidic ionic liquids. *Angew Chem Int Ed* 2010;49:5549–53.
- Ye DY, Farriol X. Improving accessibility and reactivity of celluloses of annual pulps for the synthesis of methylcellulose. *Cellulose* 2005;12:507–12.
- Ye DY, Montane D, Farriol X. Preparation and characterization of methylcellulose from annual cardoon and juvenile eucalyptus. *Carbohydr Polym* 2005;61:446–54.
- Yin X, Wu C, Zheng S, Chen Y. Design and operation of a CFB gasification and power generation system for rice husk. *Biomass Bioenergy* 2002;23(3):181–7.
- Yuan XZ, Li H, Zeng GM, Tong JY, Xie W. Sub- and supercritical liquefaction of rice straw in the presence of ethanol–water and 2-propanol–water mixture. *Energy* 2007;32:2081–8.
- Zakzeski J, Bruijninx PCA, Jongerijs AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. *Chem Rev* 2010;110:3552–9.
- Zhang SP, Yan YJ, Li TC, Ren ZW. Upgrading of liquid fuel from the pyrolysis of biomass. *Bioresour Technol* 2005;96:545–50.
- Zhang Q, Chang J, Wang TJ, Xu Y. Upgrading bio-oil over different solid catalysts. *Energy Fuels* 2006;20:2717–20.
- Zhang B, Tang X, Li X, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *Int J Hydrogen Energy* 2007a;32(13):2367–73.
- Zhang R, Wang Y, Brown RC. Steam reforming of tar compounds over Ni/olivine catalysts doped with CeO₂. *Energy Convers Manage* 2007b;48:68–77.
- Zhang Q, Wang T, Wu C, Ma L, Xu Y. Fractioned preparation of bio-oil by biomass vacuum pyrolysis. *Int J Green Energy* 2010a;7:263–72.
- Zhang XH, Wang TJ, Ma LL, Wu CZ. Aqueous-phase catalytic process for production of pentane from furfural over nickel-based catalysts. *Fuel* 2010b;89:2697–702.
- Zhang YH, Wang AQ, Zhang T. A new 3D mesoporous carbon replicated from commercial silica as a catalyst support for direct conversion of cellulose into ethylene glycol. *Chem Commun* 2010c;46:862–4.
- Zhang YM, Degirmenci V, Li C, Hensen EJM. Phosphotungstic acid encapsulated in metal-organic framework as catalysts for carbohydrate dehydration to 5-hydroxymethylfurfural. *ChemSusChem* 2010d. doi:10.1002/cssc.201000284.
- Zhang ZH, Wang Q, Xie HB, Liu WJ, Zhao ZBK. Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural by Germanium (IV) chloride in ionic liquids. *ChemSusChem* 2010e. doi:10.1002/cssc.201000279.
- Zhao XG, Lv XL, Zhao HG, Zhu YQ, Xiao WD. Study on Pd/α-Al₂O₃ catalyst for vapor-phase coupling reaction of CO with CH₃ONO to (CH₃OOC)₂. *Chin J Catal* 2004;27:125–8.
- Zhao C, Wang HZ, Yan N, Xiao CX, Mu XD, Dyson PJ, et al. Ionic-liquid-like copolymer stabilized nanocatalysts in ionic liquids: II. Rhodium-catalyzed hydrogenation of arenes. *J Catal* 2007a;250:33–40.
- Zhao HB, Holladay JE, Brown H, Zhang ZC. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* 2007b;316:1597–600.
- Zhao C, Kou Y, Lemonidou AA, Li XB, Lercher JA. Highly selective catalytic conversion of phenolic bio-oil to alkanes. *Angew Chem Int Ed* 2009;48:3987–90.

- Zhao GH, Zheng MY, Wang AQ, Zhang T. Catalytic conversion of cellulose to ethylene glycol over tungsten phosphide catalysts. *Chin J Catal* 2010a;31:928–32.
- Zhao Y, Deng L, Liao B, Fu Y, Guo QX. Aromatics production via catalytic pyrolysis of pyrolytic lignins from bio-oil. *Energy Fuels* 2010b;24:5735–40.
- Zheng JL, Kong YP. Spray combustion properties of fast pyrolysis bio-oil produced from rice husk. *Energy Convers Manage* 2010;51:182–8.
- Zhong C, Wei X. A comparative experimental study on the liquefaction of wood. *Energy* 2004;29:1731–41.
- Zhu SD, Wu YX, Yu ZN, Zhang X, Wang CW, Yu FQ, et al. Production of ethanol from microwave-assisted alkali pretreated wheat straw. *Process Biochem* 2006;41:869–73.
- Zhu YH, Kong ZH, Stubbs LP, Lin H, Shen SC, Anslyn EV, et al. Conversion of cellulose to hexitols catalyzed by ionic liquid-stabilized ruthenium nanoparticles and a reversible binding agent. *ChemSusChem* 2010;3:67–70.
- Zou S, Wu Y, Yang M, Imdad K, Li C, Tong J. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake. *Energy* 2010;35:5406–11.