

Extraction of Lignin from Biomass for Biodiesel Production

A.H. Bhat, Y.K. Dasan and Imran Khan

Abstract The renewable biorefinery concept involves transforming a pulp mill into a multipurpose biofuels, biomaterials, and biopower production facility in which these products are produced in an ecofriendly and sustainable manner. A key challenge in this process is the recovery of lignin from process streams such that it can be utilized in a variety of innovative green chemistry processes. This chapter focuses on the various methods used for the recovery of lignin and application of lignin. The study also discusses about the production of biofuel, specifically biodiesel via Lignoboost lignin pyrolysis as biofuel, steam gasification/pyrolysis of kraft lignin for biofuel, lignin hydrocracking for biofuel and hydrogenation of black liquor. Besides this, the study also throws some light on the availability of biomass, its sources, and global production of biodiesel.

Keywords Biomass · Lignin · Biodiesel

Introduction

The increasing industrialization and motorization of the world have led to a steep rise for the demand of petroleum-based fuels. Today, the fossil fuels take up 80% of the primary energy consumed in the world, of which 58% is consumed by transport sector (Savaliya et al. 2013). The major energy demand is still supplied from conventional fossil fuels such oil, coal, and natural gas. Utilization of fossil fuels over the past century and following years has drastically increased the level of greenhouse gases (GHGs) in the earth atmosphere (Talebnia 2010).

The rising concern over depleting fossil fuel and GHG limits has resulted in a high level of interest in nonconventional fuel originating from biorenewable sources in-

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cluding sugars, starches, and lignocellulosic materials (Limayem and Ricke 2012). Currently, biodiesel is the most attractive alternative to traditional fossil-based fuel, but its development and application have been hindered by the high cost of the required feedstock. However, the use of biorenewable sources considered to be the most promising candidates to replace the traditional feedstock, such as vegetable oil, could result in shortage of edible oil, and increase in food prices (Yousuf 2012).

Lignin, as a third most abundant natural polymer, has been sought for decades for productive uses. One especially attractive possibility is that of developing value-added products including biodiesel production from lignin (Saito et al. 2012). Lignin as a renewable raw material currently has technical limitations, although certain remarkable applications can be highlighted (Gosselink 2011).

The most common technique for producing biodiesel is transesterifications, which refers to a catalyzed chemical reaction of vegetable oil with an alcohol to produce fatty acid alkyl esters (biodiesel) and glycerol. The production of biodiesel from residual, agricultural biomass would have environmental benefits that far exceed its economical benefits (Yousuf 2012). Significantly, there are advantages in the use of biomass. Biomass is a renewable resource that has a steady and abundant supply, especially those biomass resources that are by-products of agricultural activity. Its use is carbon neutral, can displace fossil fuels, and helps reduce GHG emissions while closing the carbon cycle loop. As the debate on food versus fuel intensifies, biomass can provide added income to farmers without compromising the production of main food and even nonfood crops. According to International Energy Agency, biomass provides approximately 14% of the total worldwide energy needs and represents an important contributor to the world economy (Koçar and Civaş 2013).

The chapter intends to review the published investigation on lignin conversion to biodiesel and aims to present a brief overview of the available and accessible technologies for biodiesel production using renewable sources. This study also examines different feedstocks used and global markets demand for biodiesel production.

Biomass

Biomass is the name given to all the earth's living matter. It is the general term for material derived from growing plants or from animal manure. It is a rather simple term for all organic materials that stem from plants, trees, crops, and algae. The components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbon components (HC), ash, and other compounds (Demirbas 2005). The chemical composition of biomass varies among plant species, but it generally consists of approximately 50% carbon, 44% oxygen, and 6% of hydrogen (plus water), in the form of 25% lignin, and 75% of cellulose and hemicellulose (carbohydrates). Most species also contain about 5% of smaller molecular fragments such as resins, collectively known as extractives (Sims 2002).

There are five basic categories of biomass (Jansen 2012):

- a. Virgin wood from forestry or waste from forest products: palm kernel shells, woodpellets, woodchips, and sawdust.
- b. Energy crops, that is, high-yield crops grown specifically for energy applications: hybrid eucalyptus, jatropha, pongamia, and pennial grasses like *Miscanthus* and Napier grass growing on marginal land, not fit for agriculture\agricultural residues: bagasse from sugarcane, corn husks, coconut shells, and straw.
- c. Food waste, animal fat, residues from food and drink manufacturing, preparation and processing, such as used cooking oil from sunflower oil, tallow, and greases. Great examples of companies processing their waste are McDonald's (oil) and Tyson Foods (slaughter residues, fats).
- d. Industrial waste from manufacturing and industrial processes.

Different type of biomass, such as woody plants, herbaceous plants, grasses, aquatic plants, agricultural crops and residues, municipal solid waste and manures contain different amount of cellulose, hemicellulose, lignin and extractives. (Agbor et al. 2011). The value and recalcitrance of particular types of biomass depend on the chemical and physical properties of the large molecules from which it is made (McKendry 2002). The properties such as lignin content, cellulose accessibility to cellulose (CAC), and cellulose crystallinity (CC) determine overall digestibility (Agbor et al. 2011).

The biomass resource can be considered as organic matter, in which the energy of sunlight is stored in chemical bonds. When the bonds between adjacent carbon, hydrogen, and oxygen molecules are broken by digestion, combustion, or decomposition, these substances release their stored chemical energy (McKendry 2002).

Biomass produced in a sustainable way the so-called modern biomass excludes traditional uses of biomass as fuelwood and includes electricity generation and heat production, as well as transportation fuels, from agricultural and forest residues, and solid waste. On the other hand, "traditional biomass" is produced in an unsustainable way and it is used as a noncommercial source usually with very low efficiencies for cooking in many countries (Goldemberg and Teixeira Coelho 2004; Heinimö and Junginger 2009).

Biomass fuel is defined as any solid, liquid, or gaseous product derived from a wide range of organic raw materials, either directly from plants or indirectly from industrial, commercial, domestic, and forest or agricultural wastes, and produced in a variety of ways. Report of the Intergovernmental Panel on Climate Change (IPCC) shows that 400 EJ/year will be feasible from energy cropping by 2050. Together with biomass estimates from forest, cereal, and sugar cane residues (39 EJ/year), animal manures (25 EJ/year), and municipal solid wastes (3 EJ/year), then by 2050 about half the total annual global supply of primary energy could be met by biomass (Sims 2002). Biofuels production is divided into four generations depending on the nature of biomass used to produce it which is shown in Table 1.

Table 1 Classification of transportation-based biofuels

Types of biofuel	Description	Examples
First generation	Edible feedstocks	Sugarcane, sugar beet, and starch crops. oil-based crops like rapeseed, sunflower, soybean, palm oil, and waste edible oils. Starch-derived biogas
Second generation	Non-edible feedstocks	Biogas from waste and residues lignocellulosic materials (agriculture, forestry, and industry residues) biofuels from energy crops such as sorghum
Third generation	Aquatic microorganism like algae	Biodiesel from algae algal hydrogen
Fourth generation	High-solar efficiency cultivation	Carbon-negative technology: technology of the future

Biodiesel

As per the American Society for Testing and Materials (ASTM), biodiesel is a fuel consisting of monoalkyl esters of long-chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat (Hoque et al. 2011; Knothe et al. 2005; Sarin 2012). There have been a number of names applied to the ester fuels in the past decade. Technically, the esters can be called “transesterified vegetable oils (or animal fats).” In the early 1980s, the term MESO (methyl esters of soybean oil) was coined by the Volkswagen (VW) corporation. Other specific names such as RME have been used for rapeseed methyl esters. In our early work, we used the term “M-diesel” (for methanolated waste vegetable oil diesel). The Novamont Co. uses the term Diesel-BI. Recently the term “biodiesel” (for biomass-based diesel) has been widely used for ester fuels (Pop et al. 2012).

Theoretically, 1 mol triglycerides is reacting with 3 moles alcohol producing 3 moles esters and 1 mol glycerol through transesterification process with low molecular weight alcohols (Mousdale 2010) as shown in Fig. 1. This reaction is most commonly catalyzed by a homogeneous base catalyst that could be sodium hydroxide among others (Mario 2011). Methanol is the major alcohol used for transesterification process because of its most volatile fatty acid esters and also low price. However, other solvents such as ethanol, isopropanol, and butanol also can be used for this purpose (Knothe et al. 2005).

History of Biodiesel

It is believed that the term biodiesel was coined around 1984, as one the article cites the existence of a flyer from Bio-Energy (Australia) pty Ltd that promotes equipment to produce low-cost diesel fuel which is called as “Bio-Diesel” (Sarin

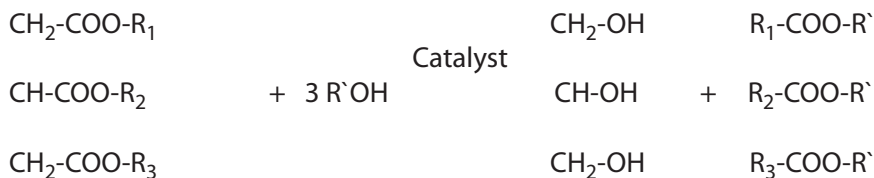


Fig. 1 Transesterification reaction. (Mario 2011)

2012). The first diesel engine was created in 1893 by a German mechanical engineer, Rudolph Diesel. The diesel engine is an internal compression-ignition engine that uses the compression of the fuel to cause ignition, instead of a spark plug for gasoline engines. As a result, a higher compression ratio is required for a diesel engine, which for the same power output (when compared to a gasoline engine), is more efficient and uses less fuel. The higher compression ratio requires the diesel engine to be built stronger so it can handle the higher pressure; consequently, the longevity of a diesel engine is generally higher than its gasoline equivalent. These vehicles therefore require less maintenance and repair overall, thus saving money (Vasudevan and Fu 2010).

The first demonstration of the diesel engine was at the 1900 World's Fair in Paris. Knothe (2001), in a book chapter, describes that the diesel engine built by the French Otto Company was tested at this event using peanut oil. It is not totally clear whether Rudolf Diesel had the idea to use peanut oil because, apparently, Diesel gives credit of this to the French government. Furthermore, he has stated the interest of French government in vegetable oil fuels for diesel engines because of its availability in their colonies in Africa, thereby eliminating the need to import liquid fuel or coal (Songstad et al. 2011).

The use of vegetable oil as an alternative fuel in diesel engine gave a sense of energy self-sufficiency to those countries producing oil crops, especially for those countries in Africa in the 1940s. During World War II, fossil fuels were diverted to the war effort, so they become hard to get and more expensive (*Solar Water Heating: A Comprehensive Guide to Solar Water and Space Heating Systems—Revised & Expanded Edition*). As a consequence of this, even Brazil prohibited the exportation of cottonseed oil so it could be used as a substituent for diesel engine. In China, tung oil and other vegetable oils were used to produce a version of gasoline and kerosene. Furthermore, prompted by fuel shortages during World War II, India conducted research on conversion of a variety vegetable oils to diesel. This interest in biodiesel was also evident in the USA where research was performed to evaluate cottonseed oil as a diesel fuel (Songstad et al. 2011). Another approach proposed at this time was the use of fatty acids' ethyl or methyl esters obtained by transesterification or alcoholysis of vegetable oils or esterification of fatty acids combined with transesterification of triglycerides (Pousa et al. 2007).

Then in 1973, the Arab oil embargo sent crude oil prices through the roof. With gas and diesel suddenly four times more expensive than before, interest in biofuels returned. But there was a dilemma: Pure vegetable oil was too thick for modern

diesel engines; it plugged injection systems and did not spray evenly into compression cylinders. Short of going back to older engine designs, two options remained: either heat the oil with an onboard system to make it less viscous (the method used by today's "Greasecars," which run on straight fryer grease) or make the oil's molecules smaller (Schmidt 2007).

The latter option led to biodiesel. In 1979, most producers chose a manufacturing method called transesterification, which the South Africans used to make fuel from vegetable oil before World War II. With that process, refiners mix the oil with alcohol in the presence of a catalyst, usually sodium hydroxide. The alcohol and fatty acids react, creating biodiesel and a by-product of glycerin. The alcohol used is usually methanol, yielding a biodiesel consisting of fatty acid methyl esters (Schmidt 2007). Since the 1980s, biodiesel plants have opened in many European countries, and some cities have run buses on biodiesel or a blend of petrol and biodiesels.

Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany, and Sweden. France launched local production of biodiesel fuel (referred to as diester) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g., public transportation) at a level of 30%. Renault, Peugeot, and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiments with 50% biodiesel are underway. During the same period, nations in other parts of the world also saw local production of biodiesel starting up: By 1998, the Austrian Biofuels Institute had identified 21 countries with commercial biodiesel projects. Hundred percent biodiesel is now available at many normal service stations across Europe. Today's diesel engines require a clean burning and stable fuel that performs well under the variety of operating conditions. Biodiesel is the only alternative fuel that can be used directly in any existing unmodified diesel engine (Abdulkareem et al. 2012).

In September of 2005, the state of Minnesota became the first US state to mandate that all diesel fuel sold in the state contains a certain part biodiesel, requiring a content of at least 2% biodiesel (B2 and up). This established that biodiesel blend fuel is no longer a choice, but a standard and mandate. On April 23, 2009, the European Union (EU) adopted the renewable energy directive (RED) which included a 10% target for the use of renewable energy in road transport fuels by 2020. It also established the environmental sustainability criteria that biofuels consumed in the EU have to comply with, covering a minimum rate of direct GHG emission saving as well as restrictions on the types of land that may be converted to production of biofuel feedstock crops (Knothe et al. 2005).

Biodiesel as an Alternative Fuel for Diesel Engine

The successful introduction and commercialization of biodiesel in many countries around the world have been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are

Table 2 Properties of biodiesel fuel and No. 2 diesel fuels. (Moser 2011)

Property	Biodiesel	No. 2 diesel
Fuel standard	ASTM D6751	ASTM D975
Lower heating value (Btu/gal)	– 118,170	– 129, 050
Density (lb/gal)	7.328	7.079
Water and sediment (% volume)	0.05 max	0.05 max
Carbon (wt. %)	77	87
Hydrogen (wt. %)	12	13
Oxygen (wt. %)	11	0
Boiling point (K)	590–625	455–625
Specific gravity (kg/L)	0.87–0.89	0.84–0.86
Cetane number	46–70	47–55
Cloud point (K)	262–289	256–265
Pour point (K)	258–286	237–243
Flash point (K)	408–423	325–350
Sulfur (wt%)	0.0000–0.0024	0.04–0.01
Ash (wt%)	0.002–0.01	0.06–0.01
Iodine number	60–135	–
Kinematic viscosity, 313 K	3.7–5.8	1.9–3.8
Higher heating value, MJ/kg	39.3–39.8	45.3–46.7
Lubricity SLBOCLE (g)	> 7000	2000–5000
Lubricity HFRR (microns)	< 300	300–600

ASTM D6751 and the European standard EN 14214, which was developed from previously existing standards in individual European countries (Knothe 2005).

While the suitability of any material as fuel, including biodiesel, can be influenced by contaminants arising from production or other sources, the nature of the fuel components ultimately determines the fuel properties. Some of the properties included as specifications in standards can be traced to the structure of the fatty esters comprising biodiesel (Knothe 2005). The biodiesel esters were characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility (Demirbas 2010) which is shown in Table 2.

Biodiesel is often used as a blend B20 (20 vol. % biodiesel and 80 vol. % conventional diesel) rather than using B100 (100 vol. % biodiesel). It is asserted that 90% of air toxics can be eliminated by using B100 whereas 20–40% are reduced using B20. A further assertion is that the risk of illness and life-threatening diseases can be reduced using biodiesel blends. Furthermore, using blends of biodiesel in oil-fired boilers can reduce NO_x and SO₂ emissions by 20% (Joshi and Pegg 2007).

Biodiesel thickens at warmer temperatures than No. 2 diesel fuel, but additives are available that will lower the pour point. Pour point is the point at which flow

of the fuel ceases. Mixing biodiesel with No. 1 diesel as is currently done with No. 2 will lower the pour point. Installing an in-tank or fuel line heater may also be needed to keep the fuel flowing in cold weather. A blend of biodiesel/diesel fuel has a lower pour point than 100% biodiesel, but gelling may still occur unless care as mentioned earlier is taken (Hofman 2003).

Advantages and Disadvantages of Biodiesel

Biodiesel has attracted considerable interest as an alternative fuel or extender for petrodiesel for combustion in compression-ignition (diesel) engines. Biodiesel is miscible with petrodiesel in any proportion and possesses several technical advantages over ultralow sulfur diesel fuel (ULSD, <15 ppm S) (Moser 2011). The most significant advantages of biodiesel given in the literature include domestic origin, reducing the dependency on imported petroleum, liquid nature-portability, readily availability, and renewability (Group and Management 2009). Life-cycle analyses have shown that the source-to-wheel CO₂ emissions from neat biodiesel combustion account for at least 60% savings with respect to petroleum diesel fuel, whereas for the most popular B20 blend it is of the order of 15–20% (Giakoumis 2013).

A number of technical advantages of biodiesel fuel: (1) It prolongs engine life and reduces the need for maintenance (biodiesel has better lubricating qualities than fossil diesel); (2) it is safer to handle, being less toxic, more biodegradable; and (3) It reduces some exhaust emissions (although it may, in some circumstances, raise others). Biodiesel is an efficient, clean, 100% natural energy alternative to petroleum fuels. Among the many advantages of biodiesel fuel, include the following: safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, nonflammable and nontoxic, reduces tailpipe emissions, visible smoke, and noxious fumes and odors. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability (Bozbas 2008).

Biodiesel can be pumped, stored, and handled using the same infrastructure, devices, and procedure usually employed for conventional diesel fuel. In fact, as biodiesel does not produce explosive vapors and has a relatively high flash point (close to 150°C), transportation, handling, and storage are safer than with conventional diesel (Yusuf et al. 2011). Biodiesel is nontoxic and degradable about four times faster than petroleum diesel. Its oxygen content improves the biodegradation process, leading to a decreased level of quick biodegradation and shows better emission parameter as compared to petroleum diesel (Moser 2011).

Despite advantages of biodiesel, the other environmental impact shows the other side. Photochemical oxidation potential (POCP) or summer smog is the result of reactions that take place between nitrogen oxides (NO_x) and volatile organic compounds (VOC) exposed to ultraviolet (UV) radiation. Higher level of POCP was directly caused by VOC (hexane) emission during the vegetable oil extraction. The other environmental impact potential, eutrophication (EP) and acidification poten-

tial (AP), has showed a significant increase compared with fossil fuels. The higher EP and AP potential in the life-cycle system of biodiesel were primarily caused by the upstream emissions of nitrate and phosphate leaching into the groundwater, and ammonia and nitric oxide (NO_x) into air from N and P fertilizer application (Hafizan and Zainura 2013). The economical drawbacks of biodiesel would be the production cost, depending in part on governmental taxes and subsidies (Black 2001).

The technical disadvantages of biodiesel/fossil diesel blends include problems with fuel freezing in cold weather, reduced energy density, and degradation of fuel under storage for prolonged periods. One additional problem is encountered when blends are first introduced into equipment that has a long history of pure hydrocarbon usage. Hydrocarbon fuels typically form a layer of deposits on the inside of tanks, hoses, etc. Biodiesel blends loosen these deposits, causing them to block fuel filters. However, this is a minor problem, easily remedied by proper filter maintenance during the period following introduction of the biodiesel blend (Bozbas 2008).

The energy efficiency of a vehicle is the percentage of fuel's energy delivered as engine output. The energy content per unit of volume measure (kilocalories per liter) of biodiesel is somewhat lower than that of petroleum diesel, so biodiesel may be less economical to use. Studies in the USA show that biodiesel contains 8% less energy per gallon than typical No. 2 diesel and 12.5% less energy per pound. The differences are due to the fact that biodiesel is slightly more dense than diesel fuel, so there are slightly more pounds in a gallon of fuel. Furthermore, all biodiesel regardless of its feedstock provides about the same amount of energy (Bucholtz 2007).

Moreover, it has been proven that the direct use of vegetable oils and/or the use of blends of the oils generally does not satisfy for direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening are obvious problems. The probable reasons for the problems and the potential solutions are shown in Table 3 (Demirbas 2008).

Sources of Biodiesel

The large-scale production of a renewable and environmentally sustainable alternative fuel faces several technical challenges that need to be addressed to make biodiesel feasible and economical. The two main concerns with any renewable fuel are raw materials and the technologies used for processing. Advances in genetic modification and other biotechnologies are resulting in new or modified feedstocks that have significantly increased the yields of alternative fuels, such as genetically modified *Clostridium* to improve alcohol production. Technological advancements are also being made to convert the feedstocks into fuels by improving techniques or developing completely new and environmentally friendly approaches to biofuel production (Vasudevan et al. 2010).

Table 3 Problems and potential solution for direct usage of vegetable oil in diesels. (Bozbas 2008)

Problem	Portable cause	Potential solution
<i>Short term</i>		
Cold weather starting	High viscosity, low octane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
Plugging and gunning of filters, lines, and injectors	Natural gums (phosphatides) in vegetable oil	Partially refine the oil to remove gums. Filter to 4 microns
Engine knocking	Very low octane of some oils. Improper injection timing	Adjust injection timing. Use higher-compression engines. Preheat fuel prior injection. Chemically alter fuel to an ester
<i>Long term</i>		
Coking of injection on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load.
Carbon deposits on piston and head of engine	Poor combustion at part load with vegetable oils	Chemically alter the vegetable oil to an ester
Excessive engine wear	Possibly free fatty acids in vegetable oils. Dilution of engine lubricating oil due to blow by vegetable oil	Increase motor oil changes. Motor oil additives to inhibit oxidation
Failure of engine lubricating oil due to polymerization	Collecting of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production. Table 3 shows main feedstocks of biodiesel. The wide range of available feedstocks for biodiesel production represents one of the most significant factors of producing biodiesel. As much as possible the feedstock should fulfill two main requirements: low production costs and large production scale. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions, and agricultural practices of any country. Selecting the cheapest feedstock is crucial to maintain the low production cost of biodiesel. In general, biodiesel feedstock can be divided into four main categories as below (Table 4) (Atabani et al. 2012):

- a. Edible vegetable oil: rapeseed, soybean, peanut, sunflower, palm, and coconut oil
- b. Nonedible vegetable oil: *Jatropha*, *Karanja*, sea mango, algae, and halophytes
- c. Waste or recycled oil
- d. Animal fats: tallow, yellow grease, chicken fat, and by-products from fish oil

Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of 1 mol of glycerol and 3 mol of fatty acids

Table 4 Sources of biodiesel feedstock. (Atabani et al. 2012; Singh and Singh 2010)

Edible oils	Nonedible oils	Animal fats	Other sources
Soybeans (<i>Glycine max</i>)	<i>Jatropha curcas</i>	Pork lard	Bacteria
Rapeseed (<i>Brassica napus L.</i>)	Mahua (<i>Madhuca indica</i>)	Beef tallow	Algae (Cyanobacteria)
Safflower	<i>Pongamia (Pongamia pinnata)</i>	Poultry fat	Microalgae (<i>Chlorellavulgaris</i>)
Rice bran oil (<i>Oryza sativum</i>)	<i>Camelina (Camelina sativa)</i>	Fish oil	Terpenes
Barley	Cottonseed (<i>Gossypium hirsutum</i>)	Chicken fat	Poplar
Sesame (<i>Sesamum indicum L.</i>)	Karanja or honge (<i>Pongamia pinnata</i>)	–	Switchgrass
Groundnut	Cumaru	–	Miscanthus
Sorghum	<i>Cynara cardunculus</i>	–	Latexes
Wheat	<i>Abutilon muticum</i>	–	Fungi
Corn	Neem (<i>Azadirachta indica</i>)	–	–
Coconut	Jojoba (<i>Simmondsia chinensis</i>)	–	–
Canola	Passion seed (<i>Passiflora edulis</i>)	–	–
Peanut	Moringa (<i>Moringa oleifera</i>)	–	–
Palm and palm kernel (<i>Elaeis guineensis</i>)	Tobacco seed	–	–
Sunflower (<i>Helianthus annuus</i>)	Rubber seed tree (<i>Hevea brasiliensis</i>)	–	–
–	Salmon oil	–	–
–	Tall (<i>Carnegieia gigantean</i>)	–	–
–	Coffee ground (<i>Coffea arabica</i>)	–	–
–	Nagchampa (<i>Calophyllum inophyllum</i>)	–	–
–	<i>Croton megalocarpus</i>	–	–

and are commonly known as triglycerides. Biodiesel contains fatty acids with different levels of unsaturation. The fuel properties of biodiesel are dependent on the amount of each fatty acid present in the feedstock. Important physical and chemical characteristics that influence the biodiesel production and its quality are mentioned below (Karmakar et al. 2010).

The source of biodiesel usually depends on the crops amenable to the regional climate. In the USA, soybean oil is the most commonly biodiesel feedstock, whereas the rapeseed (canola) oil and palm oil are the most common source for biodiesel,

in Europe and in tropical countries, respectively. A suitable source to produce biodiesel should not compete with other applications that rise prices, for example, pharmaceutical raw materials. But the demand for pharmaceutical raw material is lower than for fuel sources. As much as possible, the biodiesel source should fulfill two requirements: low production costs and large production scale. Refined oils have high production costs, but low production scale; on the other side, nonedible seeds, algae, and sewerage have low production costs and are more available than refined or recycled oils (Singh and Singh 2010).

Global Production of Biodiesel

Global demand for renewable energy continued to rise during 2011 and 2012, supplying an estimated 19% of global final energy consumption in 2011 (the latest year for which data are available), with a little less than half from traditional biomass. Useful heat energy from modern renewable sources accounted for an estimated 4.1% of total final energy use; hydropower made up about 3.7%; and an estimated 1.9% was provided by power from wind, solar, geothermal, and biomass, and by biofuels. Total renewable power capacity worldwide exceeded 1470 GW in 2012, up about 8.5% from 2011. Hydropower rose 3% to an estimated 990 GW, while other renewables grew 21.5% to exceed 480 GW. Globally, wind power accounted for about 39% of renewable power capacity added in 2012, followed by hydropower and solar photovoltaics (PV), each accounting for approximately 26% (Al Jaber et al. 2012).

Biodiesel has been in use in many countries such as USA, Malaysia, Indonesia, Brazil, Germany, France, Italy, and other European countries. However, the potential for its production and application is much more. Biodiesel has a massive potentiality to be a part of a sustainable energy mix in the future. Globally, annual biodiesel production increased from 15,000 barrels per day in 2000 to 289,000 barrels per day in 2008 as shown in Fig. 2. It is believed that, 85% of biodiesel production comes from the EU. The demand for biodiesel in European countries is expected to be up to 10.5 billion liters by 2010 (Lim and Teong 2010).

National Biodiesel Board in USA had reported production of 1.9 million liters of biodiesel in 1999 while the following year, in 2000, saw that figure increased more than tenfold to 25.4 million liters. In 2004, the Government of Philippines had made it compulsory for the incorporation of 1% of coconut biodiesel blend in diesel fuel for use in government vehicles. Elsewhere in USA, Minnesota had become the first state in the nation to mandate the use of diesel fuel with at least 2% of biodiesel blend in 2005. Biodiesel as a proven fuel was further bolstered when ASTM International published new quality specifications for biodiesel blends in 2008. Now, biodiesel blend fuel is available at many normal service stations across Europe and USA while the world biodiesel production output is estimated to be 11 million t in the year of 2008. By 2010, total biodiesel production can be as high as 20 million t. Boeing, the largest aircraft manufacturer, plans to start using biodiesel in its air car-

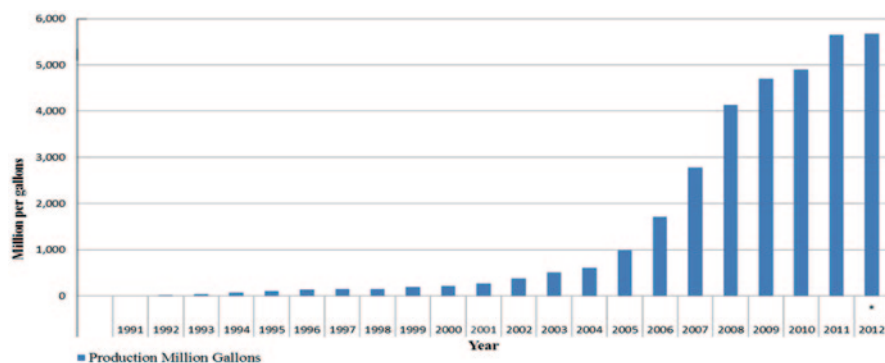


Fig. 2 World biodiesel production for the period 1991–2012

riers in 2014 which will surely increase the biodiesel demand substantially in the future (Lim and Teong 2010) (Fig. 2).

Lignin

Lignin is the most abundant natural aromatic polymer which can be found on earth. It comprises 20–30% of woody plant cell walls and by forming a matrix surrounding the cellulose and hemicellulose, it provides strength and protection to the plant (Schoemaker and Piontek 1996). The lignin heteropolymer is an integral cell wall constituent that significantly influences the physical properties of plants via its involvement in architectural support, water transport, and defense (Robinson and Mansfield 2009).

Long after Anselme Payen (1839) first described the “encrusting material” in wood, researchers were unclear about the nature of this very abundant material. Although it had a higher carbon content than the carbohydrates, its chemical nature remained obscure for a long time; indeed, it was not until about 20 years later that the term “lignin” became accepted for this material (Schulze 1857). In 1998, about 1% of all lignin generated in paper production worldwide was isolated and sold. The remaining 99% was either burned in an energy recovery step for the pulping process or disposed of in waste streams. The global production of lignin products was reported by Lin and Zhong to amount to 138,500 t/year in 1990. Extrapolating these 1% numbers leads to a worldwide production of more than 10 million t/year of available renewable raw material (Thielemans et al. 2002).

Most industrial lignin is obtained as a waste product during the paper pulping process, but it can be found in all plants like rice and straw. While cellulose is used for paper production and natural oils are mainly used in the food industry, the industrial applications of lignin are rather limited, despite its widespread availability (Thielemans et al. 2002). The recovery and usage of lignin have been studied over years to convert lignin into high value-added products. Initially, lignin has been

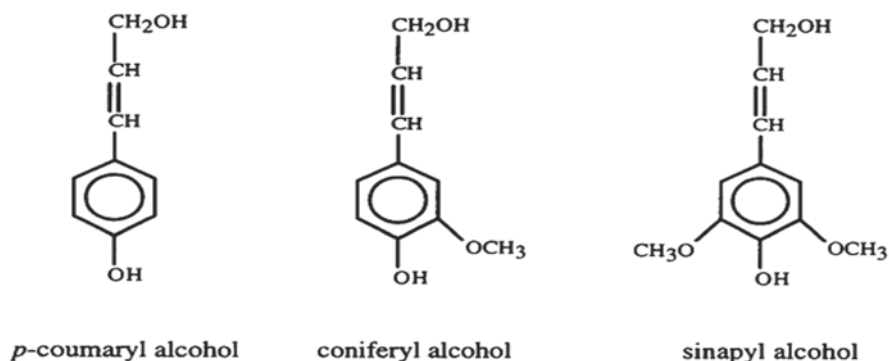


Fig. 3 Phenylpropanoid precursor of lignin. (Castillo de pilar 1997)

used as a boiler fuel in the production of octane boosters, and in biobased products and chemical production. However, the different types of lignin exist depending upon the isolation protocol and biomass sources (Gopalakrishnan et al. 2010).

Chemical and Physical Properties of Lignin

Lignin is a natural phenolic macromolecule present in the vegetal cell wall that is made up of three main phenylpropane units (monolignols), namely coniferyl alcohol (G), sinapyl alcohol (S), and *p*-coumaryl alcohol (H) (Fig. 3). Lignin structure is very complex and consists of a three-dimensional randomized net linked to hemicelluloses (LCC). The main function of lignin in the plant is as a biological barrier and asglue that retains hemicelluloses and celluloses linked shaping the cell wall.

Lignin is a highly branched and heterogeneous three-dimensional structure made up of phenylpropanoid units which are interlinked through a variety of different bonds. Lignin is biosynthesized via a plant-peroxidase-catalyzed oxidation of (methoxy-) substituted para-hydroxycinnamyl alcohols. The benzylic hydroxy groups are introduced via quinone methide intermediates (Bhanu Rekha 2013).

Complicating the molecular picture of lignin further is that native lignin chemistry can vary depending upon its origin. Plant species, plant tissue type, and the external environment all have roles in determining the chemistry of a specific lignin sample. Lignin from different plant families is known to be derived from different monolignols, and lignin is often classified according to its botanical origin. The two major classifications are gymnosperm lignin, derived mostly from coniferyl alcohol monolignols, and angiosperm lignin, derived from both coniferyl and synapyl monolignols. Each type also generally contains a small proportion of *p*-coumaryl units, though nonwoody lignins generally contain a higher amount of *p*-coumaryl units than woody lignins. There are exceptions to the rule, such as cases in which gymnosperm lignin was found to contain high amounts of synapyl alcohol units, or in which angiosperm lignin was found to be largely composed of coniferyl units.

Other phenolic monolignols have been identified, but they generally make up a much smaller portion of the lignin molecule (Fox and McDonald 2010).

Recovery of Lignins

The principal objective of isolating lignin from wood is to be used in paper production. There are two main separation processes involved for the separation of lignin such as degradation of lignin into soluble fragments and is removed by separating the solid residue from spent liquor and selectively hydrolyze polysaccharides and leave lignin along with some condensed carbohydrate deconstruction products as a solid residue (Azadi et al. 2013).

Lai and Sarkanen (1971) have published a critical review of methods for the isolating lignin. The commonly used method to isolate lignin from wood is thorough milling of the plant material, followed by extraction with dioxan±water; this material is referred to as milled wood lignin (MWL). However, the yields are usually low, and the possibility of chemical changes occurring during the isolation process must always be taken into account (Brunow 2005).

Kraft pulping method of removing lignin produces strong pulps for use in corrugated boards, liner boards, and paper bags. Besides kraft pulping, the second historically important pulping process is the sulfite process. Other wood pulping processes have been developed, though they are not usually used on an industrial scale like kraft or sulfite pulping. “Organosolv” lignin is produced by pulping wood in organic solvents with catalysts in both acidic and alkaline conditions. This process is more environmental friendly as compared to kraft or sulfite pulping due to the absence of sulfur compounds. However, solvent pulping is not currently in place on an industrial scale in North America, although one plant in Canada did use the process briefly in the 1990s (Fox and McDonald 2010).

Even though numerous methods exist to isolate lignin from plant biomass, only limited methods are recognized for lignin recovery and utilization since lignin is generally considered as a waste material and also the chemical structure of lignin changes during recovery process (Gopalakrishnan et al. 2010).

Kraft Lignin Recovery

The kraft pulping process, which uses sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to pulpwood, is the dominant pulping process in the pulp and paper industry. About 130 million t/year of kraft pulp are produced globally, accounting for two thirds of the world’s virgin pulp production and for over 90% of chemical pulp. The kraft pulping process favored over the other methods due to the ability of the process to handle almost all species of softwood and hardwood, and the favorable economics due to high chemical recovery efficiency (about 97%) give the kraft

Table 5 Sulfite-pulping conditions for lignin removal

Process	Reactive agent(s)	pH	Temperature (°C)
Acid sulfide	SO ₂ /HSO ₃ ⁻	1–2	125–145
Bisulfite	HSO ₃ ⁻	3–5	150–175
Neutral sulfite	HSO ₃ ⁻ /SO ₃ ⁻	6–7	150–175
Alkaline sulfite/anthraquinone	Na ₂ SO ₃	9–13	50–175

process and advantage over other pulping processes (Dickinson et al. 1998; Hough 1985; Singh 1980).

During kraft pulping process, lignin is removed from the wood chips and, following brown stock washing, it ends up in the spent pulping liquor (weak black liquor). This black liquor is typically concentrated from about 15–20% to 70–80% solids, with an evaporator train, and then fired into a recovery boiler for the production of steam, electricity, and inorganic chemicals (in the form of a smelt) for internal mill use (kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood). Several processes for the recovery of lignin from the black liquor are available, among them a process developed by FP Innovations and currently commercialized by NORAM, and another one, developed by STFI (now called Innventia) and licensed to Metso.

Two main approaches which are used for lignin separation in the kraft pulp process were acid precipitation and ultrafiltration (UF). Generally, precipitation is used to extract lignin from kraft black liquor, whereas UF has been used mainly to purify the lignin fraction in cooking liquor from sulfite and kraft pulp mills in order to use it as a valuable chemical product. The optimal dry substance for precipitation is reported to be 27–30%. The kraft black liquor used for precipitation is therefore commonly withdrawn after the third evaporation stage in the recovery system. The concentration of the liquor to be treated by UF is not that critical, even though the flux of the membranes is reduced as the concentration increases. This means that there is considerable freedom in the choice of liquor for treatment with UF (Wallberg et al. 2005).

Sulfite Lignin Recovery Ligninsulfonates are produced from waste liquid from softwood, using several salts of sulfurous acid (sulfites or bisulfites) to extract the lignin from wood by the sulfite-pulping procedure. The process is well known and can be carried out under several conditions as shown in Table 5. Ligninsulfonates present both hydrophobic and hydrophilic properties; they are water-soluble and chemically modified with sulfonate groups, carbohydrates, and small amounts of wood extracts and inorganic compounds. They are prepared mainly as calcium, magnesium, and ammonium salts. The procedure is less aggressive than kraft pulping, and the molecular mass of the final product is higher than kraft lignin, rendering a structure that is more similar to the original lignin.

There are various methods for isolating and purifying lignosulfonates from spent pulping liquors. For instance, the Howard process is one of the most widely used industrial processes, where calcium lignosulfonates are precipitated from spent

pulping liquor by addition of excess lime. In addition, other methods used industrially include UF and ion exclusion, which uses ion-exchange resins to separate lignin from sugars. Laboratory methods for isolating lignosulfonates include dialysis, electrodialysis, ion exclusion, precipitation in alcohol, and extraction with amines (Li 2011).

Solvent (Organosolv) Lignin Recovery

Organosolv lignins known as lignins are produced from a number of different organic solvent-based systems. Two of the most common organosolv processes are ethanol/water pulping (alcell) and pulping with acetic acid containing a small amount of mineral acid such as hydrochloric acid or sulfuric acid (acetosolv). Since 1993, carbon fibers originating from organosolv lignins have been studied where it was shown that fibers could be produced by melt spinning of hardwood acetic acid lignin isolated from spent liquor (Brodin 2009). Lignin precipitation in acid organosolv pulping is carried out by diluting the spent liquor with water, which decreases the proportion of organic solvent, reducing significantly the solubility of lignin and producing its precipitation. The precipitated lignin corresponds to the fraction of high molecular weight, the other fraction remaining in the spent liquors. Another method used to precipitate the lignin by recovering the alcohol from spent liquors in a recovery tower by vacuum. However, this procedure is usually ineffective and difficult to control, since lignin tends to precipitate as a sticky tar in the internal surfaces of the recovery tower, fouling it and reducing the effectiveness of alcohol recovery (Fernando et al. 2010). A new approach of organosolv lignin recovery, consisting of simultaneous precipitation and dissolved air flotation (DAF), is proposed. DAF offers a low-energy, low-maintenance alternative to centrifugation and filtration (Macfarlane et al. 2009).

Recovery of Lignin from Pyrolysis of Lignocellulosic Biomass

Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen. As a result, it decomposes to generate mostly vapors and aerosols, and some charcoal. The yield of the brown powder, known as pyrolytic lignin, obtained from the abovementioned method can be as high as 28 wt%, indicating that a large fraction of lignin partitions into bio-oil upon fast pyrolysis of biomass. The elemental analysis of the pyrolytic lignins obtained from several different lignocellulosic species revealed that they are composed of approximately 66% carbon, 6% hydrogen, and 27% oxygen, almost independent of the original feedstock. It is also important to note that the carbon content of the pyrolytic lignin is 9–15% and 3–9% higher than the corresponding values in the bio-oil and in MWL obtained from the same feedstock, respectively. As a result of higher carbon content, the heating value of the pyrolytic lignin is significantly higher than the

original bio-oil and the MWL (Azadi et al. 2013). Pyrolytic lignin can be recovered by precipitation since it is insoluble in water under neutral or acidic conditions (Bridgwater and Peacocke 2000).

Steam Explosion Lignin

Lignin can be recovered from steam explosion of woody materials. When wood is treated with steam at high temperature/pressure (i.e., about 180–200 °C), followed by a sudden decompression in the presence of some chemicals, a partial hydrolysis of lignin occurs. Under these conditions, a water-insoluble lignin material with a low level of carbohydrate and wood-extractive impurities results. With this procedure, the lignin itself has a somewhat reduced molecular mass because some acid hydrolysis reactions take place. This type of separation process is often combined with enzymatic hydrolysis to produce carbohydrates for fermentation (Calvo-Flores and Dobado 2010).

Applications of Lignin

Lignin from various plant material and pulping processes provides an important source of raw material that may be converted into value-added products by chemical or enzymatic means (Mattinen et al. 2008). Applications of lignin began in the 1880s when lignosulfonates were used in leather tanning and dye baths. Since then, a number of studies have been encountered to explore applications of lignin including dyes, vanilla, plastics, base exchange material for water softening, and the cleavage products of lignin from nitration, chlorinate, and caustic fusion (Gopalakrishnan et al. 2010).

The use of lignin has increased due to the high yield pulping process which includes sulfite and kraft pulping (Kutscha and Gray 1970). Sugar-free lignosulfonates from softwoods (conifers) serve as starting material to make vanillin—a flavoring for food, ice cream, and bakery goods. The anionic charges (negatively charged ions) in lignosulfonates make them good emulsifying agents or auxiliaries for preparing or stabilizing oil-in-water or wax-in-water emulsions (for example, in polishes and furniture creams or sprays) (McMillen 1967). Another major application of lignosulfonates is for mud viscosity control during deep oil well drilling. Lignosulfonates are also included in some adhesives. They act as extenders for the phenolic resins used in manufacturing particleboard, nonwoven fiber padding, and molding powders. (Browning and Perricone 1962).

In binders, about 50% of kraft lignin or lignosulfonate lignin can be added instead of phenol to phenol-formaldehyde resins without substantially modifying of the final product properties. The substitution of phenols by lignins is not only environmentally friendly but also less expensive than other binders used in the wood composite industry. Some physical and mechanical properties are modified, for ex-

ample, in novolac-type resins, the addition of lignin leads to polymeric systems with increased rigidity (Calvo-Flores and Dobado 2010).

Kraft lignins are used in some foam fire extinguishers to stabilize the foam and in printing inks for high-speed rotary presses. Kraft lignin products are generally used in high-value applications after the modification process. These include usage as emulsifying agents/emulsion stabilizers, as sequestering agents, as pesticide dispersants, as dye dispersants, as additives in alkaline cleaning formulations, as complexing agents in micronutrient formulations, as flocculants, and as extenders for phenolic adhesives. Furthermore, it can also be used as an extender/modifier, and as a reinforcement pigment in rubber compounding (Li 2011).

Production of Biodiesel from Lignin

The basic structure of all woody biomass consists of three organic polymers: cellulose, hemicelluloses, and lignin in the trunk, foliage, and bark. These three structural components are having rough formulae as $\text{CH}_{1.67}\text{O}_{0.83}$, $\text{CH}_{1.64}\text{O}_{0.78}$, and $\text{C}_{10}\text{H}_{11}\text{O}_{3.5}$, respectively. Added to these materials are extractives and minerals or ash. The proportion of these wood constituents varies between species, and there are distinct differences between hardwoods and softwoods. In general, hardwoods contain about 43 % cellulose, 22 % lignin, and 35 % hemicelluloses while softwoods contain about 43 % cellulose, 29 % lignin, and 28 % hemicelluloses (on an extractive-free basis). One of the major differences between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels from 10 to 44 % while petroleum has essentially none, making the chemical properties of biorenewables very different from petroleum. For example, biorenewable products are often more polar and some easily entrain water and can therefore be acidic (Demirbas 2009).

As one of the biorenewable resources, lignin can be converted into useful bio-fuels via biomass upgrading and biorefinery technologies. Biomass upgrading processes include fractionation, liquefaction, pyrolysis, hydrolysis, fermentation, and gasification. Upgraded bio-oil from biomass pyrolysis can be used in vehicle engines as a fuel (Demirbas 2009). The biorefinery economy is a vision for a future in which biorenewables replace fossil fuels. The transition to a biorefinery economy would require huge investment in new infrastructure to produce, store, and deliver biorefinery products to end users (Balat 2008; Demirbas 2008; Mohan et al. 2006).

LignoBoost Lignin Pyrolysis as Biofuel: One of the separation processes of kraft lignin from black liquor is called LignoBoost. The final product can be used as a fuel in power boilers. For isolation of lignin, acid precipitation was selected as the most potentially promising route. The lignin starts to precipitate at a pH of approximately 11.5, with the yield increasing to approximately 60 % of the original lignin content at pH 10. The precipitation varies according to the acid strength. As the addition of the weak acid carbon dioxide gave slightly lower yield than precipitation with sulfuric acid, for pulp mill process economy carbon dioxide was chosen

for future studies. To get purified lignin, the filtration properties of the lignin precipitate were systematically investigated by using a test filtration equipment with well-defined conditions (constant pressure, constant solid concentration of the feed and, minimized influence of sedimentation). The average specific filtration resistance of the filter cake was found to strongly depend on both precipitation pH and precipitation temperature. The large differences in filterability were shown to be caused by smaller lignin particle sizes formed at higher precipitation pH and/or at lower precipitation temperatures. Furthermore, washing the lignin after precipitation is an important step for the removal of residual black liquor and metal ions (especially sodium) (Axegård & STFI-Packforsk 2007). The filter cake, consisting of lignin, is re-dispersed and acidified again, resulting in slurry. This slurry is filtered once more and the filtrate is also brought back to the evaporation plant. However, some part of the filtrate is used for the re-dispersion of the filter cake from the first filtration. The filter cake is finally washed with the use of displacement washing. The posttreatment of the produced filter cake is, e.g., drying and pulverization (Hedlund 2010).

Pyrolysis of LignoBoost lignin extracts directly yields useful and valuable products that are currently extracted from nonrenewable fossil fuel resources (Janković 2011). Pyrolysis of lignin involves heating at 400 °C for 2 min and followed by removal of char on top heating element. The biomass samples were dropped onto the heating plate in 50 mg increments up to 1.2 g. Helium was used as a purge gas and also as a means of maintaining an inert environment. The resulting gases were fed to a condenser immersed in liquid nitrogen. At the end of the experiment, the condenser was allowed to heat back up to room temperature, and the bio-oil samples were collected (Nagy 2009).

Steam Gasification/Pyrolysis of Kraft Lignin for Biofuel

Steam gasification was carried out at atmospheric pressure in a continuous down-flow fixed-bed microreactor which operates at 600, 700 and 800 °C. The reactor was filled with a sample of accurately weighed lignin char (1–2 g) mixed with quam chips (mass ratio 19). The system was tested for leaks prior to the steam gasification run. Heating was started and when the reactor attained a temperature of –110 °C, water was fed into the reactor at the desired flow rate using a micrometering syringe pump (Eldex model A-604). The reactor had a long preheating section. Thus, there was sufficient time for the water introduced into the reactor to vaporize and to produce steam (at the gasification temperature used) before contacting the lignin char. It took approximately 25–30 min to reach the desired operating temperature. The run was continued for another 30 min until no more gas was produced from the reactor. The product leaving the reactor was condensed and separated into liquid (mainly unreacted water) and gaseous fractions. The liquid product fraction was collected in a glass trap, which was cooled with flowing tap water. The gases were collected over saturated brine. After each run, the spent lignin was removed from the reactor and weighed. The difference in combustible content of lignin before and

after the run was taken as an estimate of the lignin or char converted (Bakshi et al. 1999).

The liquid product that obtained from fast pyrolysis of biomass can be converted to value-added products such as aromatic hydrocarbons and cyclic aliphatic hydrocarbon over HZSM-5 zeolite catalyst. The experiments were conducted at atmospheric pressure using a continuous down-flow fixed-bed microreactor operated over a temperature range of 500–650 °C and weight hourly space velocity (WHSV) range of 2.5–7.5 h⁻¹ (for the lignin and acetone solution). The reactor was a 400-mm long, 11.5-mm ID (made of 316 SS) placed coaxially in a furnace. The catalyst particle size range was 500–1410 µm. The catalyst was held by a plug of quartz glass wool which was placed on a supporting mesh inside the microreactor (Bakshi et al. 1999; Bridgwater et al. 1999)

Lignin Hydrocracking for Biofuel

This material can be pyrolyzed to make a pyrolysis oil, but due to the high water content of the pyrolysis oil, often greater than 25%, high total acid number of approximately 70, and phase incompatibility with petroleum-based materials, pyrolysis oil has found little use. The pyrolytic lignin is separated from pyrolysis oil and contains potentially high-value products in the form of aromatic and naphthenic compounds. Pyrolytic lignin is a complex structure that comprises aromatic rings that are linked by oxygen atoms or carbon atoms, and can be broken into smaller segments when decarboxylated or hydrodeoxygenated and further reduced under mild hydrocracking conditions, while maintaining the aromatic ring structures (Marker and Petri 2009).

The deoxygenated light oil stream is passed to a separation process where the deoxygenated light oil is separated into an aqueous stream and an organic stream. The organic stream is passed to a hydrocracking where mild hydrocracking is performed, thereby generating a product stream. The product stream comprises aromatic and naphthenic compounds for use in gasoline or naphtha boiling range products. A small amount of diesel is produced which can be put into diesel boiling range products. The product stream can be further processed by passing the product stream to a reforming unit. The reforming unit reduces the naphthenic content and generates an aromatic rich product stream for use in gasoline (Marker and Petri 2009).

Hydrogenation of Black Liquor

Creasy and Covey have done some research on hydrogenation of kraft black liquor. The black liquor used in the experiments originated from batch kraft eucalyptus pulping. The liquor was diluted with water to give a concentration of 15.8% black liquor solids. The experiments were performed in an autoclave with a volume of 1 L. The idea was to use the water gas shift reaction (WGS reaction) as the source of

hydrogen for the liquid-phase hydrogenation. Sodium was used as a catalyst for the WGS reaction in all experiments. During the trials, the reactor was heated to 350 °C which took about 45 min. The reaction rate of the pyrolysis is rather slow during the heating period, while the WGS reaction almost reaches equilibrium. There are some ways to make the reaction rates more equal: The CO can be added when 350 °C has been reached or, e.g., borax can be used as a catalyst for the pyrolysis (Hedlund 2010).

An experimental design was constructed where experiments with and without borax was conducted, CO was added at 15, 350 °C or not at all, and the black liquor was kept at 350 °C for 20 min or quenched directly. In total, 14 experiments were carried out. After each test, the product was acidified with HCl and filtrated. Both the retentate and the filtrate were extracted with 1,1,1,tri-chloroethane. The solids from the retentate extraction composed the char fraction, while the extract from the filtrate was evaporated and the residue was added to the retentate extract. The oil fraction was formed by combining the two extract residues. The mean value of the specific energy value was 28.1 kJ/g for the chars produced and about 32.7 kJ/g10 for the oil. The tests without CO gave a low amount of oil, while the best yields were obtained when CO was added at 15 °C. For those tests, the yield increased when the reaction was continued for 20 min at 350 °C. However, for the tests where CO was added at 350 °C, the additional 20 min did not give good yields. Altogether, the hydrogenation gave four products; a gas phase (CO₂ and H₂), an aqueous phase containing most of the original sulfur and sodium, and char and oil which can be used as fuel. Thirty to 50% of the fuel value was found in the aqueous phase, which can be used if it is brought back to the weak black liquor for evaporation and finally for incineration in the recovery boiler (Hedlund 2010).

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References

- Abdulkareem A, Jimoh A, Afolabi A, Odigire J, Patience D (2012) Production and characterization of biofuel from non-edible oils: an alternative energy sources to petrol diesel
- Agbor VB, Cicek N, Sparling R, Berlin A, Levin DB (2011) Biomass pretreatment: fundamentals toward application. *Biotechnol Adv* 29(6):675–685
- Al Jaber SA, Amin AZ, Clini C, Dixon R, Eckhart M, El-Ashry M, Hamilton K (2012) RenewableS GLOBAL STATUS REPORT (Ren21), Renewable Energy Policy Network for the 21st Century, 15, Rue de Milan F-75441 Paris CEDEX 09 France, pp 1–170
- Atabani A, Silitonga A, Badruddin IA, Mahlia T, Masjuki H, Mekhilef S (2012) A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew Sustain Energy Rev* 16(4):2070–2093
- Axegård P, STFI-Packforsk A (2007) The kraft pulp mill as a biorefinery. Division Fiber, Pulp Energy and Chemicals. STFI-Packforsk P.O. Box 5604 S-114 86, Stockholm, Sweden, Annual Report, Swedish Foundation for Strategic Environmental Research, pulp and paper industry and the Swedish Energy Agency, pp 1–6

- Azadi P, Inderwildi OR, Farnood R, King DA (2013) Liquid fuels, hydrogen and chemicals from lignin: a critical review. *Renew Sustain Energy Rev* 21:506–523
- Bakshi NN, Dalai AK, Thring RW (1999) Biomass char and lignin: potential application. Department of Chemical Engineering, University of Saskatchewan, 1 IO Science Place, Saskatoon, SK S7N 5C9, University of New Brunswick, P.O. Box 4400, Fredericton, NB E3B 5A3, pp 278–282
- Balat M (2008). Biodiesel fuel production from vegetable oils via supercritical ethanol transesterification. *Energy Sour Part A* 30(5):429–440
- Bhanu Rekha V (2013) Enhancing the absorbency of bagasse through enzymatic delignification. *J Fash Technol Text Eng*. doi:10.4172/jfite.1000101
- Black A (2001) Globalization and restructuring in the South African automotive industry. *J Int Dev* 13(6):779–796
- Bozbas K (2008) Biodiesel as an alternative motor fuel: production and policies in the European Union. *Renew Sustain Energy Rev* 12(2):542–552. doi:http://dx.doi.org/10.1016/j.rser.2005.06.001
- Bridgwater A, Peacocke G (2000) Fast pyrolysis processes for biomass. *Renew Sustain Energy Rev* 4(1):1–73
- Bridgwater A, Meier D, Radlein D (1999) An overview of fast pyrolysis of biomass. *Organ Geochem* 30(12):1479–1493
- Brodin I (2009) Chemical Properties and Thermal Behaviour of Kraft Lignins, PhD dissertation, KTH Royal Institute of Technology School of Chemical Sciences and Engineering Department of Fibre and Polymer Technology Division of Wood Chemistry and Pulp Technology, ISBN 978-91-7415-406-1, SE-100 44 Stockholm Sweden
- Browning W, Perricone A (1962) Lignosulfonate drilling mud conditioning agents. SPE-AIME 37th Annual Fall Mtg. in Oct, 7–10
- Brunow G (2005) Methods to reveal the structure of lignin. *Biopolym Online*. doi:10.1002/3527600035.bpol1003
- Bucholtz EC (2007) Biodiesel synthesis and evaluation: an organic chemistry experiment. *J Chem Educ* 84(2):296
- Calvo-Flores FG, Dobado JA (2010) Lignin as renewable raw material. *ChemSusChem* 3(11):1227–1235
- Castillo del Pilar M (1997) Degradation of pesticides by *Phanerochaete chrysosporium* in solid substrate fermentation. Swedish University of Agricultural Sciences (SLU), Sweden
- Demirbas A (2005) Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Prog Energy Combust Sci* 31(2):171–192
- Demirbas A (2008) Effect of alkali on liquid yields from the pyrolysis of olive oil. *Energy Sour Part A* 30(11):1060–1064
- Demirbas A (2010) Biorefineries: for biomass upgrading facilities. In: *Biorefinery*, pp 75–92
- Dickinson J, Verrill C, Kitto J (1998) Development and evaluation of a low-temperature gasification process for chemical recovery from kraft black liquor. Paper presented at the International Chemical Recovery Conference
- Fatih Demirbas M (2009). Biorefineries for biofuel upgrading: a critical review. *Appl Energy* 86:151–161
- Fernando EF, Vallejos EM, Area MC (2010) Lignin recovery from spent liquors from ethanol-water fractionation of sugar cane bagasse. *Cellulose Chem Technol* 44:311–318
- Fox SC, McDonald AG (2010) Chemical and thermal characterization of three industrial lignins and their corresponding lignin esters. *BioResources* 5:990–1009
- Giakoumis EG (2013) A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of unsaturation. *Renew Energy* 50:858–878
- Goldemberg J, Teixeira Coelho S (2004) Renewable energy—traditional biomass vs. modern biomass. *Energy Policy* 32(6):711–714
- Gopalakrishnan K, Teixeira Coelho S (2010) Renewable energy—traditional biomass Biowastes and Biomass, pp 247–274. Edited by Samir KK, Rao YS, Tian CZ, Buddhi PL, Tyagi RD, Kao CM, ISBN (print): 978-0-7844-1089-9, American Society of Civil Engineers

- Gosselink R (2011). Lignin as a renewable aromatic resource for the chemical industry, Mini-symposium organised by Wageningen UR Lignin Platform, Wageningen, Netherlands.
- Group UNEPBW, Management UNEPIPfSR (2009) Towards sustainable production and use of resources: assessing biofuels: UNEP/Earthprint
- Hafizan C, Zainura NZ (2013) Biofuel: advantages and disadvantages based on Life Cycle Assessment (LCA) perspective. *J Environ Res Dev* 7(4):1444–1449
- Hedlund T (2010) High Pressure and Temperature Conversion of Lignin and Black Liquor to Liquid Fuels, Master's Thesis within the Innovative and Sustainable Chemical Engineering programme, Department of Energy and Environment Division of Heat and Power Technology CHALMERS UNIVERSITY OF TECHNOLOGY Göteborg, Sweden
- Heinimö J, Junginger M (2009) Production and trading of biomass for energy—an overview of the global status. *Biomass Bioenerg* 33(9):1310–1320
- Hofman V (2003) Biodiesel Fuel. NDSU Extension Service, North Dakota State University of Agriculture. Applied Science and US Department of Agriculture cooperating, Fargo, North Dakota
- Hoque ME, Singh A, Chuan YL (2011) Biodiesel from low cost feedstocks: the effects of process parameters on the biodiesel yield. *Biomass Bioenerg* 35(4):1582–1587
- Hough G (1985) Chemical recovery in the alkaline pulping processes: a project of the Alkaline Pulping Committee of the Pulp Manufacture Division: Tappi ISBN: 0898520460, Atlanta, GA, USA: TAPPI, c1985, 312 p
- Janković B (2011) The comparative kinetic analysis of Acetocell and LignoBoost® lignin pyrolysis: the estimation of the distributed reactivity models. *Bioresour Technol* 102(20):9763–9771. doi:<http://dx.doi.org/10.1016/j.biortech.2011.07.080>
- Jansen RA (2012) Second generation biofuels and biomass: essential guide for investors, scientists and decision makers. Wiley-VCH, Weinheim
- Joshi RM, Pegg MJ (2007) Flow properties of biodiesel fuel blends at low temperatures. *Fuel* 86(1):143–151
- Karmakar A, Karmakar S, Mukherjee S (2010) Properties of various plants and animals feedstocks for biodiesel production. *Bioresour Technol* 101(19):7201–7210
- Knothe G (2001), Historical perspective on Vegetable-oil based Diesel fuels. *INFORM* 12, 1103–1107.
- Knothe G (2005) Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process Technol* 86(10):1059–1070
- Knothe G, Van Gerpen JH, Krahl J (2005) The biodiesel handbook, vol 1. AOCS press, Champaign
- Koçar G, Civaş N (2013) An overview of biofuels from energy crops: current status and future prospects. *Renew Sustain Energy Rev* 28(0):900–916. doi:<http://dx.doi.org/10.1016/j.rser.2013.08.022>
- Kutscha NP, Gray JR (1970) The potential of lignin research
- Lai Y-Z, Sarkanen KV (1971) Isolation and structural studies. In: Sarkanen KV, Ludwig CH (eds) *Lignins: occurrence, formation, structure and reactions*. WileyInterscience, New York, pp 165–240
- Li J (2011) Isolation of lignin from wood
- Lim S, Teong LK (2010) Recent trends, opportunities and challenges of biodiesel in Malaysia: an overview. *Renew Sustain Energy Rev* 14(3):938–954
- Limayem A, Ricke SC (2012) Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. *Prog Energy Combust Sci* 38(4):449–467
- Macfarlane A, Prestidge R, Farid M, Chen J (2009) Dissolved air flotation: a novel approach to recovery of organosolv lignin. *Chem Eng J* 148(1):15–19
- Mario (2011) A Comparison Between Raw Material and Technologies for a Sustainable Biodiesel Production Industry, Economic Effects of Biofuel Production, Dr. Marco Aurelio Dos Santos Bernardes (ed.), ISBN: 978-953-307-178-7, InTech, Croatia
- Marker TL, Petri JA (2009) Gasoline and diesel production from pyrolytic lignin produced from pyrolysis of cellulosic waste: google patents
- Mattinen M-L, Suortti T, Gosselink R, Argyropoulos DS, Evtuguin D, Suurnäkki A, et al. (2008) Polymerization of different lignins by laccase. *BioResources* 3(2):549–565
- McKendry P (2002) Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 83(1):37–46

- McMillen JM (1967) US department of agriculture forest service forest products laboratory Madison, WIS
- Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & Fuels* 20(3):848–889
- Moser BR (2011) Biodiesel production, properties, and feedstocks. In: *Biofuels*. Springer, New York, pp 285–347
- Mousdale DM (2010) Introduction to biofuels. CRC, Boca Raton
- Moser (2011) Biodiesel production, properties, and feedstocks. *In Vitro Cell Dev Biol Plant* 45:229–266 (2009)
- Payen A (1839) Memoir on the composition of the tissue of plants and of woody material. *Comptes Rendus* 9:149
- Pop A, Ceclan R, Ceclan M (2012) Biodiesel from waste vegetable oils. *Chem Eng Trans* 29:1177–1182
- Pousa GP, Santos AL, Suarez PA (2007) History and policy of biodiesel in Brazil. *Energy Policy* 35(11):5393–5398
- Robinson AR, Mansfield SD (2009) Rapid analysis of poplar lignin monomer composition by a streamlined thioacidolysis procedure and near-infrared reflectance-based prediction modeling. *Plant J* 58(4):706–714
- Saito T, Brown RH, Hunt MA, Pickel DL, Pickel JM, Messman JM, et al. (2012) Turning renewable resources into value-added polymer: development of lignin-based thermoplastic. *Green Chem* 14(12):3295–3303
- Sarin A (2012) Biodiesel: production and properties. Royal Society of Chemistry
- Savaliya M, Dhorajiya B, Dholakiya B (2013) Recent advancement in production of liquid biofuels from renewable resources: a review. *Res Chem Intermed* 41:475–509. doi:10.1007/s11164-013-1231-z The volume no. is 41, pages 475–509
- Schmidt CW (2007) Biodiesel: cultivating alternative fuels. *Environ Health Perspect* 115(2):86–91
- Schoemaker HE, Piontek K (1996) On the interaction of lignin peroxidase with lignin. *Pure Appl Chem* 68:2089
- Sims RE (2002) *The brilliance of bioenergy: in business and in practice*: Earthscan. ISBN: 190291628X, Published by James & James (Science Publishers) Ltd., 35-37 William Road London NW1 3ER, UK
- Singh RP (1980) Kraft pulp bleaching and recovery process: google patents
- Singh S, Singh D (2010) Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: a review. *Renew Sustain Energy Rev* 14(1):200–216
- Songstad D, Lakshmanan P, Chen J, Gibbons W, Hughes S, Nelson R (2009) Historical perspective of biofuels: learning from the past to rediscover the future. *In Vitro Cell Dev Biol Plant* 45:189–192
- Talebnia F, Karakashev D, Angelidaki I (2010) Production of bioethanol from wheat straw: an overview on pretreatment, hydrolysis and fermentation. *Bioresour Technol* 101(13):4744–4753
- Thielemans W, Can E, Morye S, Wool R (2002) Novel applications of lignin in composite materials. *J Appl Polym Sci* 83(2):323–331
- Vasudevan PT, Fu B (2010) Environmentally sustainable biofuels: advances in biodiesel research. *Waste Biomass Valor* 1(1):47–63
- Vasudevan PT, Gagnon MD, Briggs MS (2010) Environmentally sustainable biofuels—the case for biodiesel, biobutanol and cellulosic ethanol *Sustainable biotechnology Sources of Renewable Energy*. Singh OV, Harvey SP (eds) 2010, XVII, 323 p, ISBN: 978-90-481-3295-9, Springer eBook, pp 43–62
- Wallberg O, Holmqvist A, Jönsson A-S (2005) Ultrafiltration of kraft cooking liquors from a continuous cooking process. *Desalination* 180(1):109–118
- Yousuf A (2012) Biodiesel from lignocellulosic biomass—prospects and challenges. *Waste Manage* 32(11):2061–2067. doi:http://dx.doi.org/10.1016/j.wasman.2012.03.008
- Yusuf N, Kamarudin S, Yaakub Z (2011) Overview on the current trends in biodiesel production. *Energy Convers Manage* 52(7):2741–2751