

University of Belgrade  
Technical Faculty Bor

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# PROCEEDINGS

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## XXIII International Conference Ecological Truth

Editors

Radoje V. Pantovic

Zoran S. Marković

*EcoIst '15*

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Hotel "PUTNIK", Kopaonik, SERBIA  
17-20 June 2015

UNIVERSITY OF BELGRADE  
TECHNICAL FACULTY BOR



**XXIII International Conference  
"ECOLOGICAL TRUTH"**

*Eco-Ist'15*

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Edited by

**Radoje V. PANTOVIC  
and  
Zoran S. MARKOVIC**

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## PYROLYSIS OF LIGNOCELLULOSIC BIOMASS

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### ABSTRACT

Limitations and exhaustions of energy sources (e.g. fossil fuels) have resulted in taking major steps in sustainable plans for rational using of resources that exist today and finding new, alternative energy resources. Biomass is renewable energy resource which can be grown where climatic conditions are appropriate. Bio-oil as one of the major products obtained from the pyrolysis of lignocellulosic biomass has a number of industrial applications. After upgrading it is possible to use bio-oil as fuel for transport. Pyrolysis temperature is the main factor that affects the transfer of heavy metals in the volatile fraction of pyrolysis products.

**Key words:** pyrolysis, lignocellulosic biomass, bio-oil.

### INTRODUCTION

World is facing many economical and environmental problems related to the application and consumption of energy. As a result of significant growth of population and rapid industrial and economical development, the consumption of energy is increasing despite high energy prices and many negative impacts on the environment. Limitations and exhaustions of energy sources (e.g. fossil fuels) have resulted in taking major steps in sustainable plans for rational using of resources that exist today and finding new, alternative energy resources [1,2].

Significant environmental pollution is the result of the consumption of fossil fuels (oil, coal, natural gas). Burning of fossil fuels releases harmful gases (CO, CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, CH<sub>4</sub>) which are linked to the global warming[3].

### BIOMASS

Biomass is any organic matter derived from plants. It includes phytomass and zoomass [4]. Biomass is renewable energy resource which can be grown where climatic conditions are appropriate [5]. Biomass includes agricultural and forestry residues, aquatic and marine biomass and wastes (municipal solid waste, municipal sewage sludge, animal, industrial and urban organic waste, ect)[5,6].

Main polymers of biomass are cellulose, hemicelluloses and lignin[7]. Biomass usually contains 40-50 wt.% cellulose, 20-40 wt.% hemicellulose and 10-40 wt.% lignin. Besides these polymers, biomass is made of inorganic material (ash) and extractives[8]. Cellulose is linear polymer composed of D-glucopyranose linked with  $\beta$ -1,4glycosidic linkage[9]. Hemicellulose is branched polymer composed of pentoses, hexoses and/or urgonic acids[10]. Lignin consist of aromatic polymers (synthesized from phenylpropanoid precursors) and inhibits absorption of water through cell wall [9,10].

## **BIOFUELS**

Biofuels are gaseous or liquid fuels derived from renewable materials such as biomass. Biofuels include "first" and "second generation biofuels". Raw material for making first generation biofuels is sugar, starch and vegetable oil. Their production has impact on the food supply [11]. Non-edible lignocellulosic biomass can be used as feedstock for production of second generation biofuels[12-15]. There are also "third generation biofuels" and "fourth generation biofuels" which are made from algae and vegetable oil, respectively[16].

## **METHODS FOR CONVERSION OF BIOMASS**

Processes for converting biomass to energy and fuels can be divided on thermochemical and biochemical[17]. Biochemical conversion uses enzymes and microorganisms for conversion of biomass, while heat is used for thermochemical conversion[3].

Combustion, pyrolysis, gasification and liquefaction are main thermochemical conversion processes [18]. Combustion (the burning of biomass in air) is used to convert chemical energy from biomass into heat, mechanical power or electricity. This process is performed at temperature around 800-1000°C[19]. Gasification is production of gaseous fuels from solid fuels at temperature range of 800–1300°C. Main product, producer gas, is composed of H<sub>2</sub>, CO, CH<sub>4</sub> and other impurities such as CO<sub>2</sub>, nitrogen, sulfur, alkali compounds and tars[5]. Oxygen is widely used gasification agent. Beside it, steam, air, CO<sub>2</sub>, O<sub>2</sub> can be used as well [3]. This process can be viewed as a special form of pyrolysis which is performed at higher temperatures for production of gas (syngas). Direct liquefaction is performed at low-temperature and high pressure for breaking down biomass into small fragments in water or another solvent[18]. Thermochemical decomposition of biomass in the absence of oxygen is called pyrolysis [20]. Main products of pyrolysis are gas, liquid and char[21]. Depending upon operating parameters (temperature, vapor residence time, size of feed particles, rate of biomass heating, sweeping gas flow rates, mineral matter contents, and initial moisture), characteristics of biomass and pyrolysis type, the obtained amount of products vary. Gaseous and char products are dominant at higher and lower temperatures, respectively[22]. Pyrolysis liquid product is called pyrolysis oil or bio-oil, [23]. CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> do not condense during cooling and they represent gas products, while solid product (char) is made of carbon, oxygen and hydrogen [3].

## TYPES OF PYROLYSIS

Pyrolysis can be divided into conventional slow pyrolysis (carbonization), fast pyrolysis and flash pyrolysis. This classification is based on the operating conditions[24].

Pyrolysis that is performed on temperature from 400–600°C with heating rate of 0.1–1°C/s and residence time from minutes to hours is called slow pyrolysis[25]. Charcoal, the main product, can be used for domestic cooking, as raw material for production of different chemicals, activated carbon, absorbents, ect[21].

Fast pyrolysis involves high liquid yield [25]. Decomposition of biomass happens very quickly and mostly vapors and aerosols are generated, as well as some charcoal and gas[26]. The essential features of a fast pyrolysis process for producing liquids are:dry feedstock (less than 10%), small particles (less than 3 mm), short hot vapor residence times of typically less than 2 s to minimize secondary reactions, carefully controlled pyrolysis reaction temperature of around 500°C to maximize the liquid yield for most biomass,very high heating rates, rapid removal of product char to minimize cracking of vapors andrapid cooling of the pyrolysis vapors to give the bio-oil product[25, 26-28].Typical yields of bio-oil, char and gaseous products of 60–70%, 12–15% and 13–25%, respectively[29]. Bio-oil obtained this way is considered as second generation bio-fuel [30].

Flash pyrolysis is used for production of solid, liquid and gaseous product and with this process yield of 75% of bio-oil can be achieved[31].

Table 1 represents ranges of main operating parameters for pyrolysis and relative distribution of products [31, 32].

**Table 1.** Range of the main operating parameters and products distribution for pyrolysis processes[31, 32]

Pyrolysis process	Solid residence time [s]	Heating rate [K s <sup>-1</sup> ]	Particle size [mm]	Temperature [K]	Product yield (%)		
					Oil	Char	Gas
Slow	450-550	0,1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1	850-1250	50	20	30
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

Besides these three types of pyrolysis there are also:flash hydro-pyrolysis, solar flash pyrolysis, ultra-rapid (ultrafast) pyrolysis, hydro-pyrolysis, vacuum pyrolysis and methano-pyrolysis. However, the researches for producing bio-oil by vacuum flash pyrolysis, microwave assisted pyrolysis, and plasmapyrolysis are recently reported[6, 33].

## APPLICATION AND UPGRADING OF BIO-OIL

Bio-oil (main product of fast pyrolysis) is composed of polar organics (about 75-80 wt%) and water (about 20-25 wt%)[27]. These compounds are derived from cellulose, hemicellulose and lignin depolymerization and fragmentation[34]. Organic compounds include acids, alcohols, aldehydes, esters, ketones, phenols, lignin-derived oligomers, furans, alkenes, sugars, nitrogen components, guaiacols, syringols,

miscellaneous oxygenates[6, 35]. Inorganics in bio-oil are: Ca, Si, K, Fe, Al, Na, S, P Mg, Ni, Cr, Zn, Li, Ti, Mn, Ln, Ba, V, Cl, etc[6].

Some industrial application of bio-oil are combustion fuel in boiler, combustion in diesel engines, transportation fuel (after upgrading), production of anhydro-sugars, chemicals, adhesives [35].

Bio-oil has a higher water content (15-30 wt.%), low and corrosive pH (<3), higher oxygen content (35-40 wt.%) and lower heating value (HHV of 16-19 MJ/kg) compared with petroleum heavy fuel oil[18]. Much lower heating value of bio-oil compared with that for fossil fuel is because of many oxygenated compounds in bio-oil and significant portion of water[32].

Current techniques used for bio-oil upgrading are: hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, supercritical fluids (SCFs), emulsification and esterification [35, 36].

### INFLUENCE OF PYROLYSIS TEMPERATURE ON YIELDS OF BIO-OIL

Many researchers studied pyrolysis of rapeseed (*Brassica napus*L.)[37-40], rapeseed cake[41-43], straw and stalk of the rapeseed plant[44], sunflower (*Helianthus annuus*L.) pressed bagasse[45-49], agricultural residues of sunflower[50], corncob (*Zea mays* L.)[51-55]and corn stover[56].Fig. 1 represents maximum bio-oil yield from pyrolysis of different biomass.

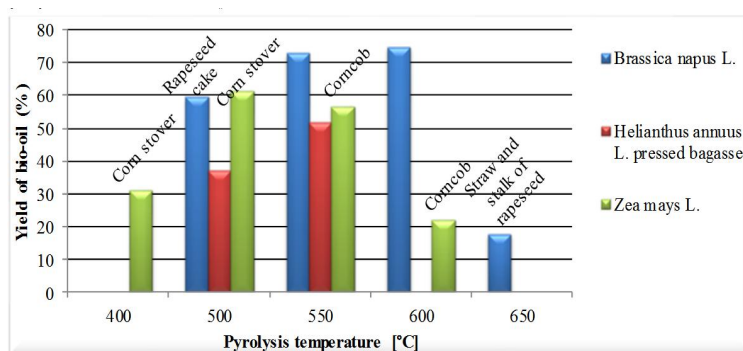


Figure 1. Maximum yield of bio-oil obtained by pyrolysis of different plant material

### PYROLYSIS AS A TECHNIQUE FOR TREATING HEAVY METAL CONTAMINATED PLANT MATERIAL

Many concerns are associated with phytoremediation, such as handling and disposal of the biomass enriched with heavy metals. Result of combustion of biomass is volatilization of heavy metals, and this is why other techniques (like pyrolysis) should be explored. Advantages of this method are: reduction of volume and weight of heavy metal contaminated biomass; energy recovery; production of char/ash which contains heavy metals [57]. Pyrolysis experiments were made on different biomass contaminated with heavy metals [57-61]. Table 2 represents these results.

**Table 2.** Heavy metal behavior (presence in obtained bio-oil) after pyrolysis of different biomass

Metal	350°C	400°C	450°C	500°C	550°C	600°C	Plant material	Ref
Cd	ND	/	ND	10 %**	ND	40 %**	Sunflower	[57]
	<1 ppm	ND	0.7%	ND	13%	ND	<i>Salix fragilis</i> – stems and leaves	[59]
	0.2%	ND	3.2%	ND	10.5%	ND	<i>Salix fragilis</i> – stems with hot-gas filter	[60]
Cu	<5 ppm	ND					<i>Salix fragilis</i> – stems and leaves	[59]
Pb	<1 ppm	ND	/	ND	/	ND	<i>Salix fragilis</i> – stems and leaves	[59]
	<1.9%	ND	<1.9%	ND	3%	ND	<i>Salix fragilis</i> – stems with hot-gas filter	[60]
Zn	ND	/	ND	/	ND	<1%*	Sunflower	[57]
	<1%	ND					Willow - leaves and branches	[58]
	0.2%	ND	<1%**	ND	0.4 %	ND	<i>Salix fragilis</i> – stems and leaves	[59]
	0.5%	ND	0.2 %	ND	0.5 %	ND	<i>Salix fragilis</i> – stems with hot-gas filter	[60]

\*\* – no detectable concentration of heavy metals; ND- no data; \* – gaseous fraction; \*\* – non- and condensable pyrolysis fractions; \*\*\* - mixture of stems and leaves (filter experiments)

## CONCLUSION

The economic development of many countries around the world has increased the need for alternative energy sources due to the lack of fossil fuels (limited quantity; greenhouse gas emissions that cause global warming) and the increase in fuel prices. Biomass is considered to be one of the alternative energy sources that seems to be the most promising because it does not contribute to a net increase in CO<sub>2</sub> levels in the atmosphere and contains small amounts of sulfur, nitrogen and ash.

Bio-oil as one of the major products obtained from the pyrolysis of lignocellulosic biomass has a number of industrial applications. After upgrading it, it is possible to use bio-oil as fuel for transport.

The best scope for obtaining bio-oil from rapeseed, sunflower and corn is from 500-600°C. The maximum yield of bio-oil of rapeseed (*Brassica napus* L.) of 75% was achieved at a temperature of 600°C, rapeseed cake gave 59.7% of bio-oil at 500°C, and from the straw and stalk of rapeseed was obtained 18% of bio-oil at 650°C. The maximum yield of bio-oil (52.1%) from the sunflower pressed bagasse (*Helianthus annuus* L.) was obtained at a temperature of 550°C, and sunflower oil cake gave 48.69% of bio-oil on 550°C. The agricultural residue of the sunflower gave the maximum yield of 30% of bio-oil at 550°C. The maximum yield of bio-oil from corn cobs (*Zea mays* L.) was achieved at a temperature of 500°C and it was 61%, and at a temperature of 550°C was obtained 56.8% of bio-oil, while for the corn stover gave the maximum yield of bio-oil of 61.6% at 500°C.

Pyrolysis temperature is the main factor that affects the transfer of heavy metals in the volatile fraction of pyrolysis products. Copper, lead and zinc are retained in the solid fraction of pyrolysis products in the temperature range of 350-600°C, while cadmium shows volatility at temperatures over 450°C and its volatility increases with increasing temperature.

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