

ISOLATION OF PHENOL AND PHENOLIC COMPOUNDS FROM FAST PYROLYSIS BIO-OIL OF FORESTRY RESIDUE

Alma Jazbinšek, Viktor Grilc, Ljudmila Fele Žilnik
National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia,
alma.jazbinsek@ki.si

The use of renewable energy sources is becoming increasingly necessary, if we are to achieve the changes required to address the impacts of global warming. Biomass is the most common form of renewable energy, widely used in the third world until recently, but nowadays its use is increasing also in the western world. The energy from biomass can be obtained by various techniques, such as combustion or upgrading into a more valuable fuel, gas or oil. It can also be transformed into a source of higher value products for the chemical industry by using a thermochemical method, such as pyrolysis. Solid biomass can be liquefied by pyrolysis, hydrothermal liquefaction, or other thermochemical technologies. Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam. Often fast pyrolysis is utilized, in which organic materials are rapidly heated to 450 - 600°C in the absence of air. Under these conditions, organic vapours, pyrolysis gases and charcoal are produced. The vapours are condensed to bio-oil. Typically, 70-75 wt % of the feedstock is converted into oil.

For pyrolysis nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, corncobs, tea waste and nut shells to energy crops such as miscanthus and sorghum. Forestry wastes such as bark and thinnings and other solid wastes, including sewage sludge and leather wastes, have also been studied by other authors. But most of the research work has been done on wood.

The liquid product of biomass pyrolysis, known as bio-oil or pyrolysis oil, is a complex mixture of several hundreds of organic compounds that exhibits a wide range of chemical functionality. Bio-oil is dark brown, free-flowing organic liquid that is comprised of highly oxygenated compounds. It is very viscous, relatively unstable and susceptible to aging. Chemically, bio-oil is a complex mixture of water, guaiacols, catechols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics.

The aim of our work was the isolation of individual fractions of phenolic compounds from bio-oil. In our experiments the bottom phase of the bio-oil obtained by pyrolysis of forestry residue was used.

Isolation of phenolic compounds from the bottom phase was carried out. Phenolic compounds were separated from the bio-oil by liquid-liquid extraction using alkali and organic solvents. The identification of the phenolic compounds in raw bio-oil was carried out by gas chromatography coupled to a mass spectrometer (GC/MS). When the phenolic compounds were identified, the analyses of GC eluted compounds (quantifications) were performed on the Carlo Erba Instruments GC 8000 (GC/FID). The isolation of the phenolic compounds was performed in three stages. The first stage was rinsing of bio-oil with water, while in the second stage the extraction of phenolic compounds from the bottom phase, dissolved in solvent, by using alkali solution was carried out. The third stage represented solvent reextraction of phenolic compounds. The objective of our work in the future is an optimization of individual stages and the separation of individual fractions by distillation process.

1. Introduction

BIOCOUP is a European project that unites different universities, research centres and industrial companies. BIOCOUP project is supported through the six framework programme for research and technological development:

- SP1: Primary Liquefaction. Improve the quality of the primary oil and reduce production costs.
- SP2: Bio-liquid upgrading. Research and development of various upgrading-deoxygenation technologies.
- SP3: Co-processing in standard refinery. Assessment of co-processing upgraded bio-liquids in standard refinery equipment.
- SP4: Conversion. Identification and technology development to obtain discrete target compounds from the bio-liquids.
- SP5: Scenario analysis. Identification and assessment of the most promising biomass-to-refinery chain(s) on basis of predicted technical, economical and LCA-performances.
- SP6: Transversal activities. Coordination of the project, analytical support to all the partners in the consortium and dissemination of the knowledge generated within BIOCOUP.

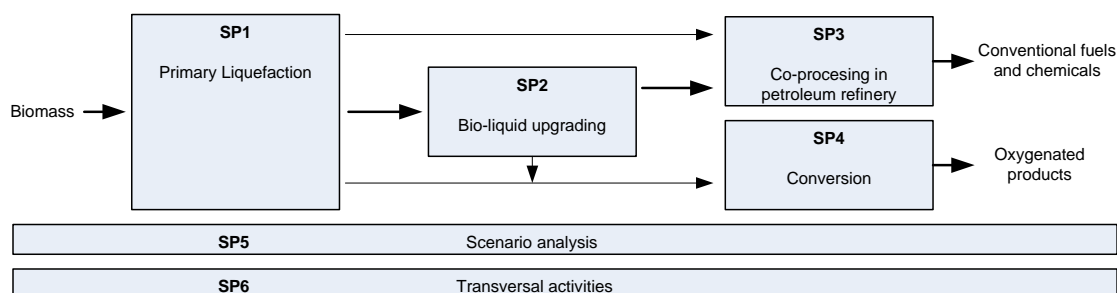


Figure 1. BIOCOUP sub-projects structure

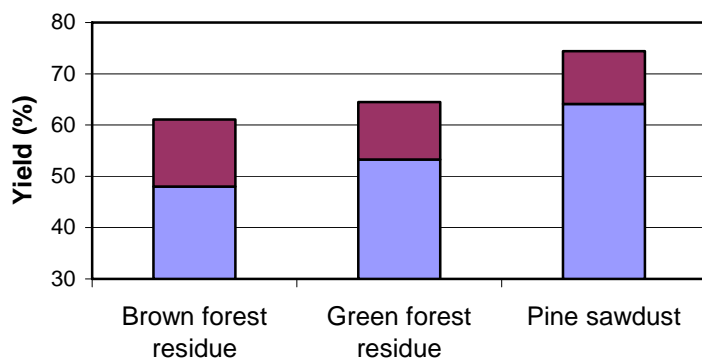
Bio-oil, gained from biomass with fast pyrolysis, can be used as fuel. It can also be transformed into a source of higher value products for the chemical industry. Final upgraded products must be suited to be co-processed in existing refinery units.

Bio-oil differs from fossil fuels over large content of water, oxygen and corrosiveness. These properties make the co-processing of bio-oil in standard refineries impossible. Bio-oil needs to be upgraded. One of the upgrading processes considered within BIOCOUP is hydrodeoxygenation (HDO) of fast pyrolysis oil (PO). In this process, oxygen is removed from oxygenated hydrocarbons in the form of water using hydrogen and a catalyst.¹

National Institute of Chemistry, Slovenia is engaged in a sub-project SP4 with a purpose to identify and develop technology to obtain different phenolic compounds or fractions from the bio-oil.

Various types of biomass can be used to produce bio-oil. For the experiments described in this paper we used bio-oil produced with fast pyrolysis at about 520°C from the forest residue. The forestry residue pyrolysis liquid separates immediately after a condensation to a polar, liquid bottom phase (80-90 wt %) and a hydrophobic viscous top phase (10-20 wt %).

The amount and composition of the top phase are affected by the feedstock (wood species, amount of needles, feedstock storage time), pyrolysis and recovery of product.² Liquid yields (organic+water) from forestry residue ranged from 59 to 64 wt % of dry feed and the yield for pine sawdust was about 74 wt % (Figure 2).



Water	13,1	11,2	10,3
Organic	48	53,3	64,1

Figure 2: Liquid yields for pyrolysis liquids from brown and green forestry residue and pine.²

The water-soluble fraction (22 wt % of water) of green forestry residue liquid contained about 1 wt % of alcohols (methanol) and 6 wt % of low-molecular-mass carboxylic acids, of which the share of acetic and formic acids was 90%. The bottom phase contained also aldehydes, ketones, phenolic compounds, sugars, lignins, etc.

2. Experimental

The objective of our work is the isolation of individual fractions of phenolic compounds from bio-oil, gained with pyrolysis of the forestry residue.

The qualitative analyses of the bottom phase of bio-oil obtained by pyrolysis of the forestry residues were performed on Agilent GC (6890N)-MSD (5973N) chromatograph with split injection. We identified a number of phenolic compounds and the final quantitative determinations were performed on Carlo Erba Instruments GC 8000 (GC/FID).

A feasible separation route to isolate phenolic fractions from bio-oil was investigated. The addition of a certain amount of water to bio-oil was used to remove the water from the bottom phase of the bio-oil. The phase split was initiated and two phases occurred, namely bottom phase, very viscous, dark phase that represented 25% of the total amount and upper aqueous phase, transparently brown, that represented 75%.

The formed bottom phase was dissolved in a solvent and further contacted with a basic solution. After the separation of the phases, the evaporation of the major amount of solvent took place.

The phenolic compounds that remained in the basic phase were recovered by acidifying the solution, followed by solvent re-extraction.

3. Results and discussion

As it was mentioned, we identified a number of different phenolic compounds in the bottom phase of the bio-oil. Figure 3 shows the largest peaks of phenolic compounds.

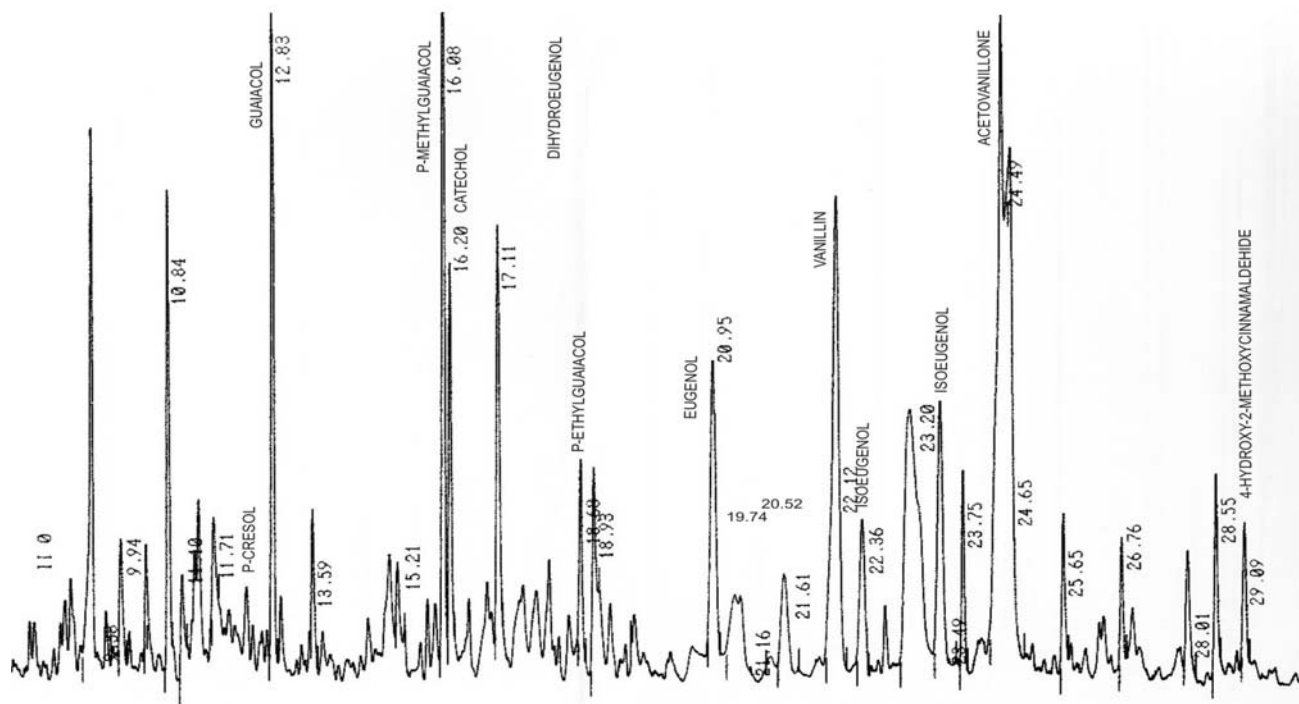


Figure 3: Chromatogram of the bottom phase of bio-oil

The peak of acetovanillone on Figure 3 is partial covered with another peak of levoglucosan. After an addition of water to the phase, this sugar and other water soluble substances partitioned to an aqueous phase, and the phenolic compounds were concentrated in the bottom organic phase (Figure 4)

When the new formed bottom phase was contacted with the basic solution, the phenolic compounds, with lower pK_A were concentrated in an aqueous phase. The majority of the phenolic compounds remained in an organic phase.

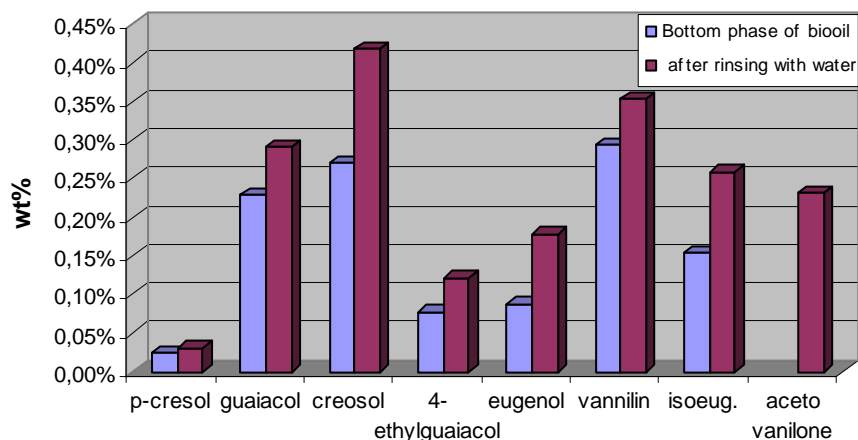


Figure 4: Comparison of phenolic compounds concentrations in the lower phase before and after washing out with water.

Figure 5 shows a chromatogram of a mixture of phenolic compounds after the contact with the basic solution and partial evaporation of a solvent. The comparison of the Figures 3 and 5 shows that after the contact with the basic solution and partial evaporation of the solvent mainly the phenolic compounds remained and all other substances were almost removed.

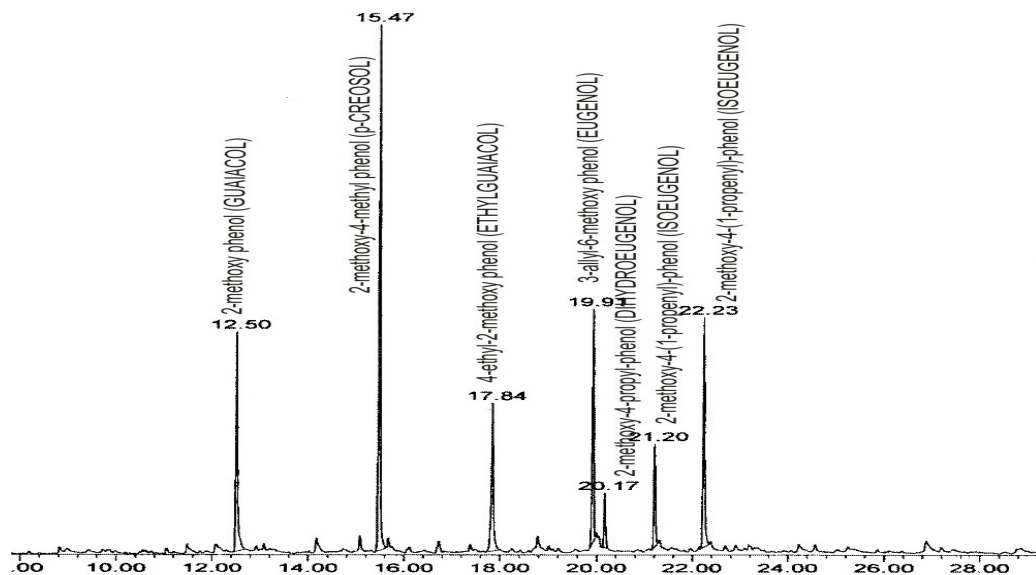


Figure 5: Chromatogram of a mixture of phenolic compounds after the contact with the basic solution and partial evaporation of the solvent

Figure 6 shows the increase of a concentration of phenolic compounds after contact with basic solution and partial evaporation of solvent.

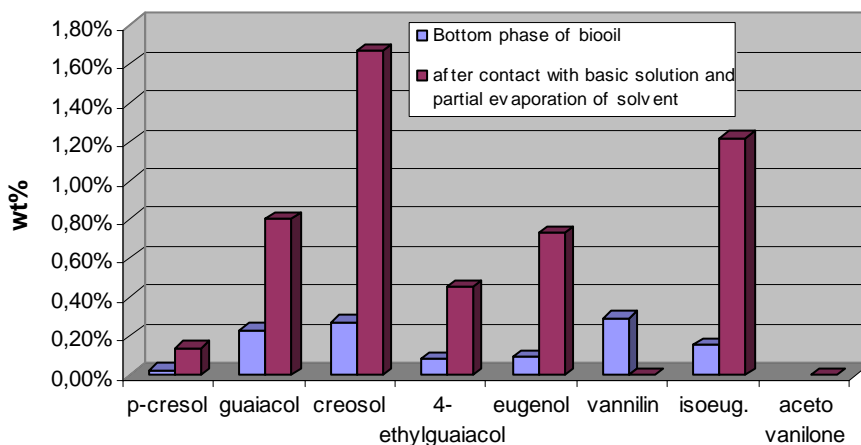


Figure 6: Comparison of phenolic compounds concentration between un-processed bottom phase of bio oil and a mixture of phenolic compounds after the contact with the basic solution and partial evaporation of solvent.

The investigation of a feasible separation route to isolate phenolic compounds or fractions is in progress. The objective of our future work is an optimization of individual stages and the separation of individual fractions by distillation process.

5. References

1. F.M. Mercadera, A. Ardiyantib, A. Gutierrezc, S. Khromovad, E. Leijenhorste, S. Kerstena, K. Hogendoorna, W. Prinse, M. Groeneveld; Upgrading of bio-liquids for co-processing in standard refinery units; 19th EU Contest for Young Scientists, Valencia, Spain, September 2007
2. A. Oasmaa, E. Kuoppala and Y. Solantausta, Fast pyrolysis of forestry residue. 2. Physicochemical Composition of product Liquid, Energy & Fuels 2003,17, 433-443

Acknowledgement

The financial support from the EU project BIOCUP 518312 is gratefully acknowledged.