Hydrothermal liquefaction of Thessaly's agricultural wastes targeting high quality bio-crude production

D. Liakos[1,2], A. Dimitriadis[1], V. Dagonikou[1], K. Triantafyllidis[2], A. Kokkalis[3], S. Bezergianni[1]

[1]Centre for Research & Technology Hellas (CERTH), Chemical Process & Energy Resources Institute (CPERI), Thessaloniki, 6km Charilaou-Thermi, 57001, Greece
[2]Aristotle University of Thessaloniki (AUTH), Department of Chemistry, University Campus, 54124 Thessaloniki, Greece
[3]Green Innovative Company (GRINCO), 17th km Larissa-Thessaloniki Rd, Industrial Area, 41004, Greece
Keywords: hydrothermal liquefaction, bio-crude oil, wastes, biomass.
Presenting author email: dliakos@certh.gr

The constant increment of energy demand, as well as the environmental pollution and the global warming, have led the scientific community in search of petroleum renewable alternatives. Aiming at this direction, the utilization of Thermo-Chemical conversion technologies in waste biomass are currently being thoroughly studied (Patel, 2016). A promising technology for biomass conversion towards liquid fuels is Hydro-Thermal Liquefaction (HTL), as it constitutes a flexible technology with many benefits compared to other technologies. Agricultural residues appear as suitable materials for producing biobased intermediates but the application of HTL for their valorization is currently restricted due to the low liquid yield (Dimitriadis, 2017).

This study will focus on the development and the investigation of the hydrothermal liquefaction technology for converting residual agricultural biomass from the Thessaly region in Greece to bio-crude, with simultaneous utilization of crude glycerol as co-solvent from biodiesel production by-products. According to other studies, it is estimated that the potential agricultural residues in Greece is 4.9 MT dry mass per year, while most of these materials are produced in Thessaly plains. Moreover, the majority of these residues include wheat straw (24%) and olive branches (20%) (Christou, 2013), rendering these two feedstocks worth examining.

Wheat straw and olive branches composition is presented in Table 1 (Petersen, 2009, Fonseca, 2020). Both are typical examples of lignocellulosic biomass, consisting mainly of cellulose, hemicellulose, and lignin. Ash content is low, while extractives appear to be a significant proportion, especially in the case of wheat straw. On the other hand, lignin is relatively low in wheat straw, compared to the olive tree branches as well as to other types of lignocellulosic biomass. These differences in biomass composition appear to be of main interest as they may define the final bio-crude oil yield and its composition (Dimitriadis, 2017). Glycerol, on the other hand, is a polyalcohol produced in significant quantities as the byproduct of the transesterification step in biodiesel refineries. Crude glycerol is an alkaline mixture composed from glycerol, salts, as well as free fatty acids and fatty acid methyl esters, which are trapped valuable biodiesel compounds (Pedersen, 2015).

Table 1. Composition analysis of wheat straw (Petersen, 2009) and olive tree branches (Fonseca, 2020)

Composition (%)	Wheat Straw	Olive Tree Branches
Cellulose	35.0	36.5
Hemicellulose	22.3	21.3
Lignin	15.6	24.1
Extractives	20.9	12.8
Ash	6.5	2.5

The main goal of this study is the production of bio-crude via HTL of wheat straw as well as of olive tree branches. To that purpose, the effect of HTL main parameters in bio-crude yield was investigated for both types of biomass in terms of maximizing bio-oil production. The examined parameters are reactor temperature (300°-420 ˚C), reaction time (15-60 min) and the water/glycerol ratio of solvent. The liquefaction process is examined in both subcritical and supercritical water conditions. All the experiments are conducted at the Centre for Research & Technology Hellas (CERTH) in a bench top, high-pressure stirred batch reactor with internal volume of 250 mL. This reactor is coupled with a J type thermowell for heating and a U type cooling coil for rapid temperature dropping and is monitored via an online computer.

At first, both types of biomass are air-dried for one week and then milled and sieved at particle size of 185-1000 μm (Figure 1). During the HTL tests, the reactor is filled with milled biomass and deionized water (or mix with glycerol) according to the desired feed/solvent ratio. Once the reactor is flushed with nitrogen to remove air,

Figure 1. Olive tree branches (left) and wheat straw (right)

it is pressurised with nitrogen at a particular pressure to ensure that the solvent remains liquid during the HTL process. Finally, the reactor is heated to the desired temperature where it is kept for 15-60 min before cooling down.

After the reactor cooldown, the gas products are collected to be analyzed with GC and the reaction mixture is vacuum filtered to recover the liquid product, while the solids are thoroughly washed with water and acetone. The solids (biochar) are air and oven dried and stored for further characterization and analysis. The liquid product, which consists of an aqueous phase and an organic phase, defined as bio-crude, is analyzed via HPLC and GC-MS for the determination of its composition.

According to the literature, bio-crude production is enhanced but with limited fuel quality properties at higher subcritical reaction temperatures, while repolymerization occurs favoring biochar formation (Dimitriadis, 2017). Supercritical conditions are also expected to boost oil yield as the contents of biomass are more easily liquefied. Moreover, crude glycerol has the potential to improve biomass conversion and according to Pedersen et al (2015) there is synergistic effect between biomass constituents and glycerol especially at supercritical conditions, enhancing lignin depolymerization to small oligomers and monomers. As a result, the aim of this work is to provide useful experimental data on the optimal range of the HTL operating conditions, reaction time and biomass/glycerol ratio that favor high bio-crude yield with controlled/optimized properties.

Moreover, HTL is a technology that produces bio-crude oil with low heteroatoms content (oxygen, nitrogen) and so, there is an increased H/C ratio with higher hydrocarbons content and consequently greater heating value liquid product. According to literature, the oil is expected to contain acids, furans, ketones and phenolics and oxygenated aromatics derived from biomass carbohydrates and lignin, respectively, with carbon atoms in range of C_6 to C_{10} which is suitable for transportation fuel production (Pedersen, 2017).

Finally, biochar constitutes the HTL product that contains most of the minerals from biomass and heavy organic compounds. Therefore, conducting an analysis over metals content of solids can define the inorganic elements proportions that are being transferred from biomass to biochar and can be recovered for further commercial and industrial use. Also, a comparative analysis between a crop residue (wheat straw) and a woody biomass residue (oil tree branches) will be conducted that can assist in better understanding the reactions that take place during hydrothermal liquefaction of agricultural biomass and create the pathway that leads to final products.

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: “AgroFUCHEr”).

References

Madhumita Patel, Xiaolei Zhang, Amit Kumar (2016), «Techno-economic and life cycle assessment on lignocellulosic biomass thermochemical conversion technologies: A review», Renewable and Sustainable Energy Reviews 53, 1486-1499

Athanasios Dimitriadis, Stella Bezergianni (2017), «Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review», Renewable and Sustainable Energy Reviews 68, 113-125

Mirsini Christou (2013), Energy potential of agricultural, livestock and forest residues in Greece, ENERGY FROM BIOMASS, Center for Renewable Sources and Energy Saving, Available at: http://docplayer.gr/11572912-Energeiako-dynamiko-agrotikon-ktinotrofikon-kai-dasikon-ypoleimmaton-stin-ellada.html

Thomas H. Pedersen, Lukas Jasiunas, Luca Casamassima, Shashank Singh et al. (2015), «Synergetic hydrothermal co-liquefaction of crude glycerol and aspen wood», Energy Conversion and Management 106, 886-891

Mai Østergaard Petersen, Jan Larsen, Mette Hedegaard Thomsen (2009), «Optimization of hydrothermal pretreatment of wheat straw for production of bioethanol at low water consumption without addition of chemicals», Biomass and Bioenergy 33, 834-840

Bruno Guedes Fonseca, Soledad Mateo, Ines Conceicao Roberto, Sebastian Sanchez et al. (2020), «Bioconversion in batch bioreactor of olive-tree pruning biomass optimizing treatments for ethanol production», Biochemical Engineering Journal 164, 107793