

Hydrothermal biofuels for the valorization of agroforestry pruning

I. Makaridis¹, D. Liakos¹, K. Moustakas², S. Vakalis¹

¹ Energy Management Laboratory, Department of Environment, University of the Aegean, Mytilene, Lesvos, 81100, Greece

² Unit of Environmental Science & Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, 15780 Athens, Greece

INTRODUCTION

The gradual environmental degradation which has proven to be the result of human activity presupposes the finding of a new framework for the acquisition of energy which will support the appropriate techniques for its correct application. Under this condition, investigating the possibilities of already existing waste-to-energy (waste-to-energy) would be a great advantage as it would become possible to produce energy and high-value products while simultaneously improving both the energy issue and waste management. For this reason, the work focuses on the research of the possibilities and the utilization of the waste lignocellular biomass of olive pruning through hydrothermal treatment. Hydrothermal carbonization (HTC) and liquefaction (HTL) experiments were performed in two reactor types, the PPL Lining Hydrothermal Autoclave Reactor and the Parr 4570 Stirred Reactor Series. For the HTC experiments, the highest concentration of COD and phenols was observed in the 200°C experiment in the presence of 6ml of water, while in the HTL experiments at the temperature of 300°C. The reaction conditions in the experiment at 225°C (8ml water) revealed secondary production of phenols. The pH measurements for the HTC experiments showed the HTC 200°C (6ml water) experiment below 4 as the most acidic, while the conductivity was highest in the HTC 200°C (8ml water) experiment. In HTL experiments the decrease in conductivity follows the increase in pH. Also, the increase in calorific value does not follow the increase in the amount of Hydrochar produced. A re-increase in Hydrochar was observed in the 225°C (10ml water) experiment. Of the HTC experiments, the HTC 225°C experiment (6ml water) has the highest calorific value, while in the HTL experiments, the 325°C experiment.

METHODS

HTC reactor experiments:

Hydrothermal treatment was carried out using the PPL Lining Hydrothermal Autoclave Reactor type. The experiments carried out in the specific reactor were six (6) in total and concerned two (2) different temperatures of 200°C and 225°C respectively. Then, using a Parr 4570 Stirred Reactor Series hydrothermal reactor, another three (3) single experiments were done at (3) different temperatures of 300°C, 325°C and 350°C, which were much higher than those of the first reactor experiments. The thermochemical processes carried out within the two reactors resulted in the production of high value products such as liquid Liquor (Bio-oil or Bio-crude), solid Hydrochar and syngas.

HHV analysis:

The Parr 6400 Automatic Isoperibol Calorimeter (Figure 2) was used to determine the highest calorific value (HHV). Laboratory use of the machine requires an oxygen supply of 99.5%, nitrogen supply at 80 psi and deionized water. Before starting calorific measurement of Hydrochar solids, a Pre-test was carried out. Specifically, a quantity of benzoic acid was initially measured in order to verify the correct operation of the calorimeter. The recorded measurement of benzoic acid was found to be 26.3950 MJ/kg close to the reported verification value of 26.454 MJ/kg.

COD and TPC analysis:

The COD determination is a two-step method, digestion and determination based on Colorimetric Analysis. The reagents were prepared in Vial vials to which 2.8ml of Silver Sulphate (catalyst) and then 1.2ml of Potassium Dichromate (strong oxidizer) were added with a small gradient to ensure two distinct layers of these until the addition of the sample to be analyzed. Similarly, the analysis of the total phenolic content was done by implementing the Folin method.



Fig. 1. Image of the Parr 4570 Stirred Reactor



Fig. 2. Parr 6400 Bomb Calorimeter

RESULTS AND DISCUSSION

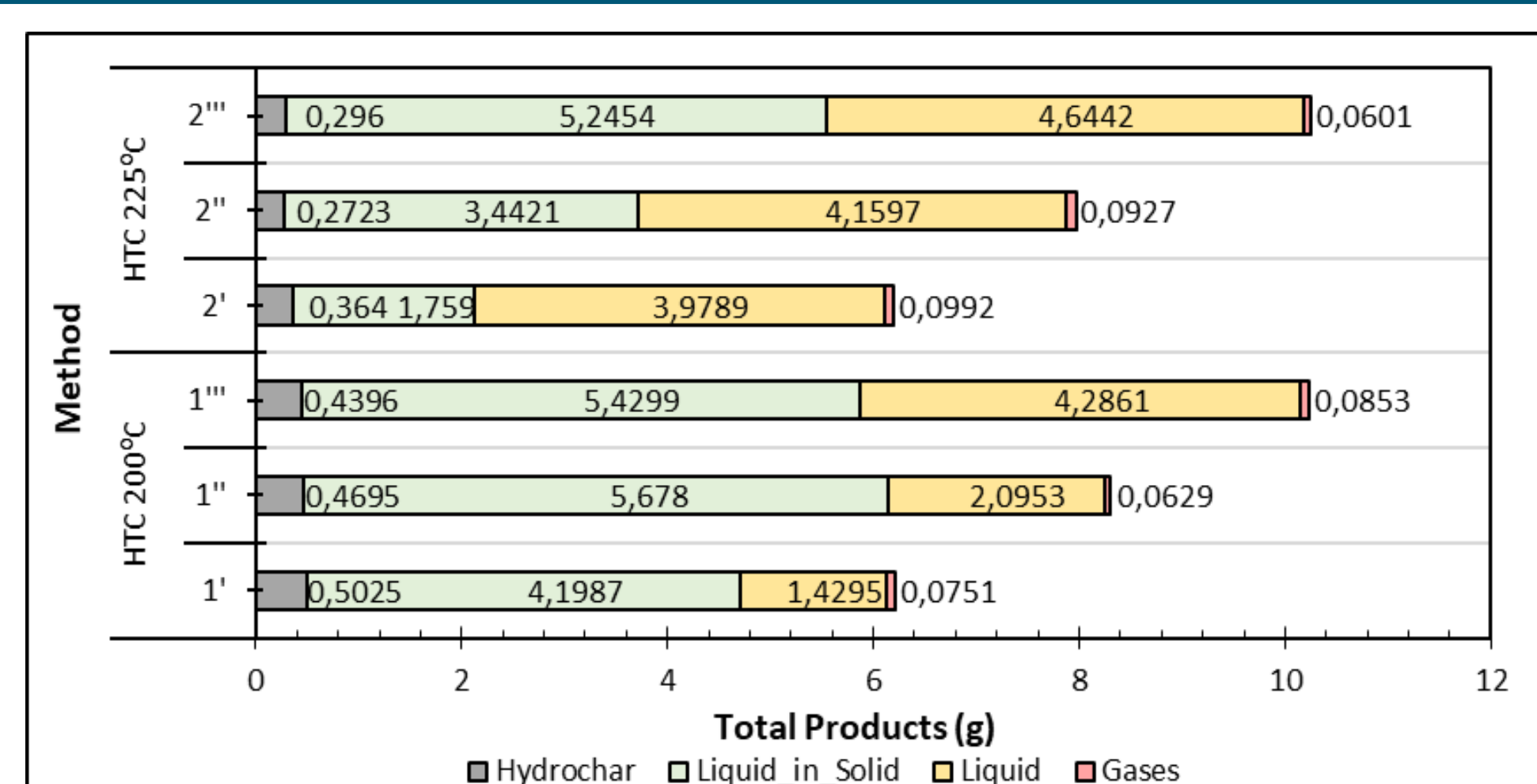


Fig 2. Product masses of hydrothermal carbonization (HTC)

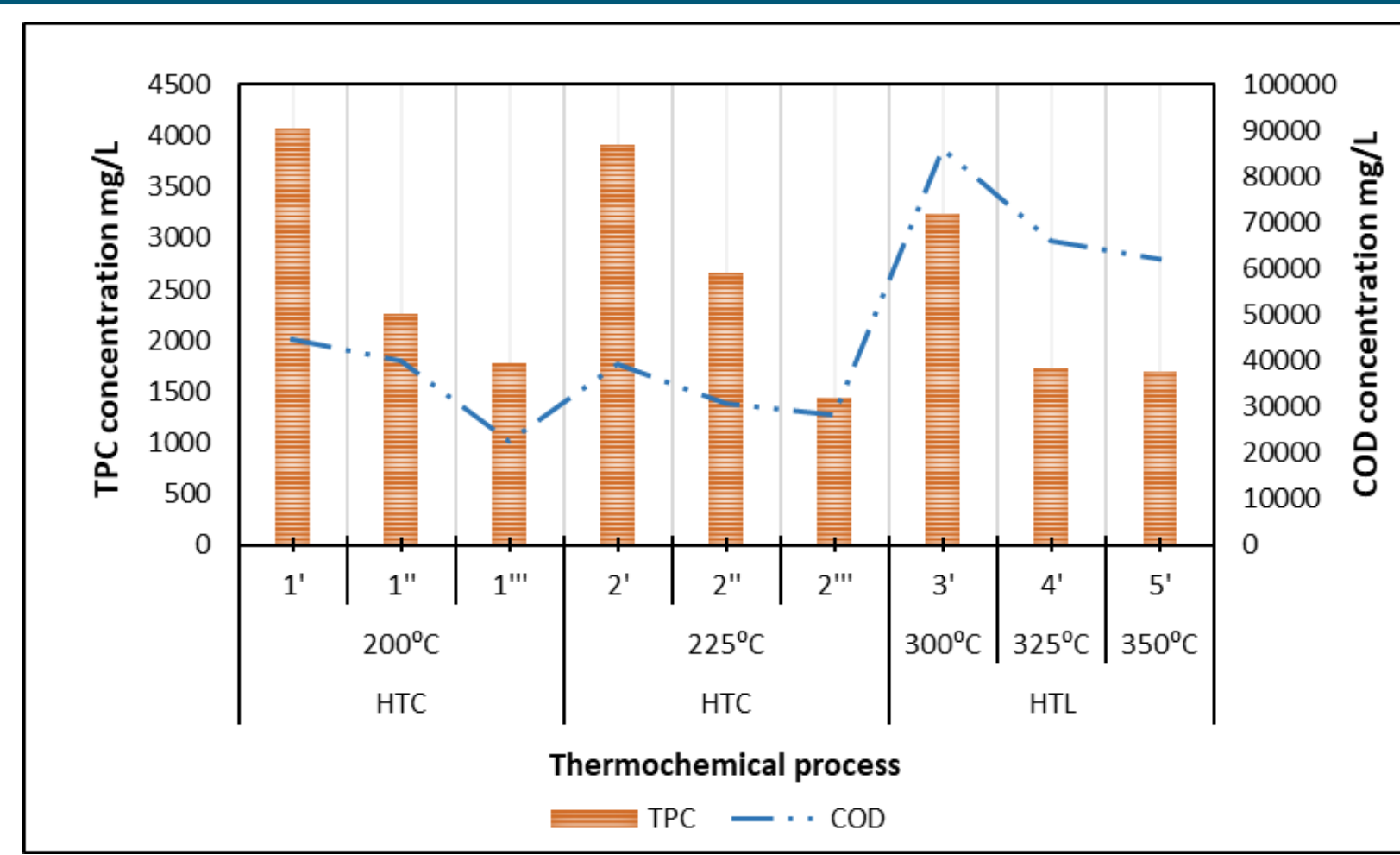


Fig. 4. COD of the produced liquid samples

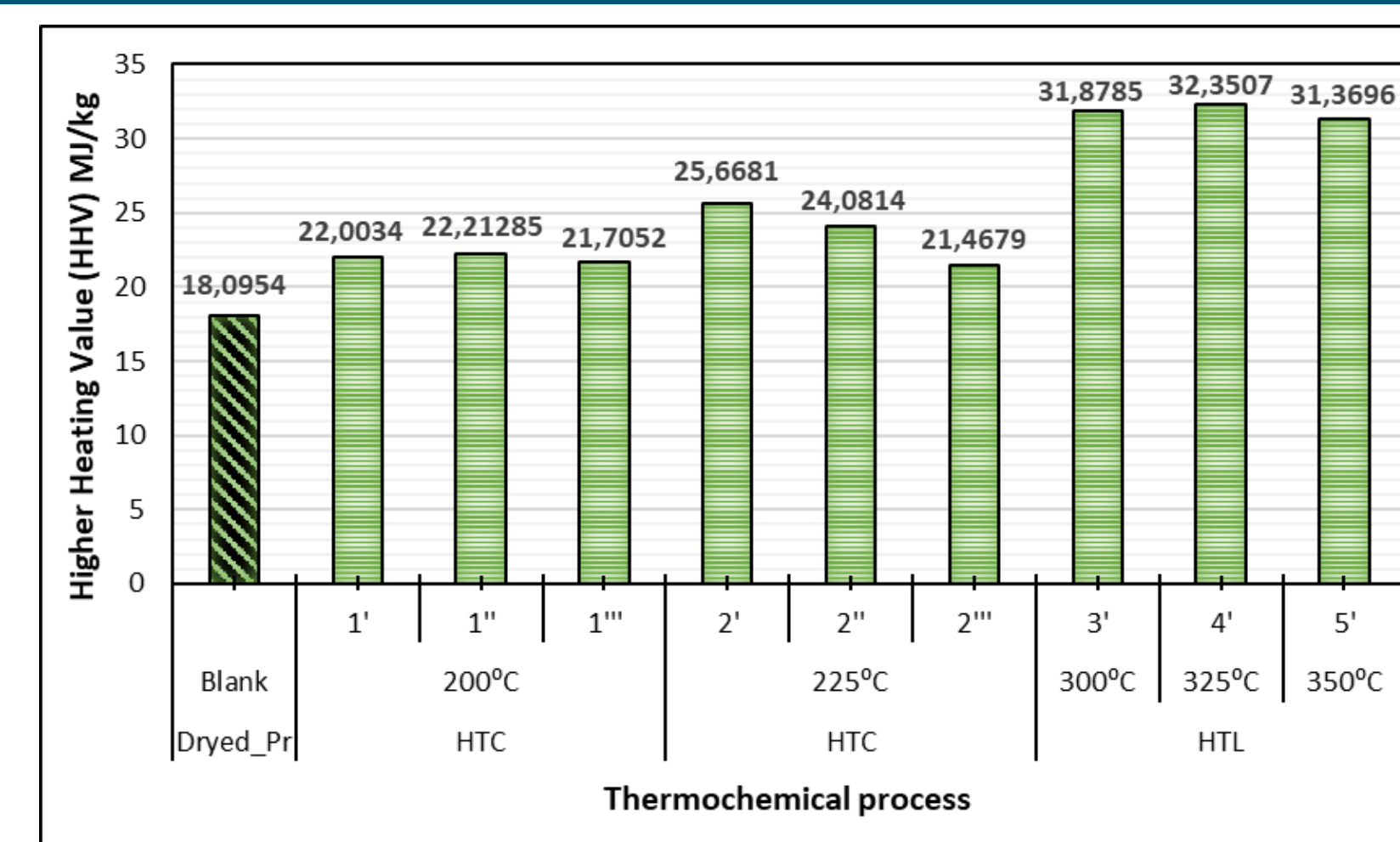


Fig. 5. HHV of the produced hydrochar

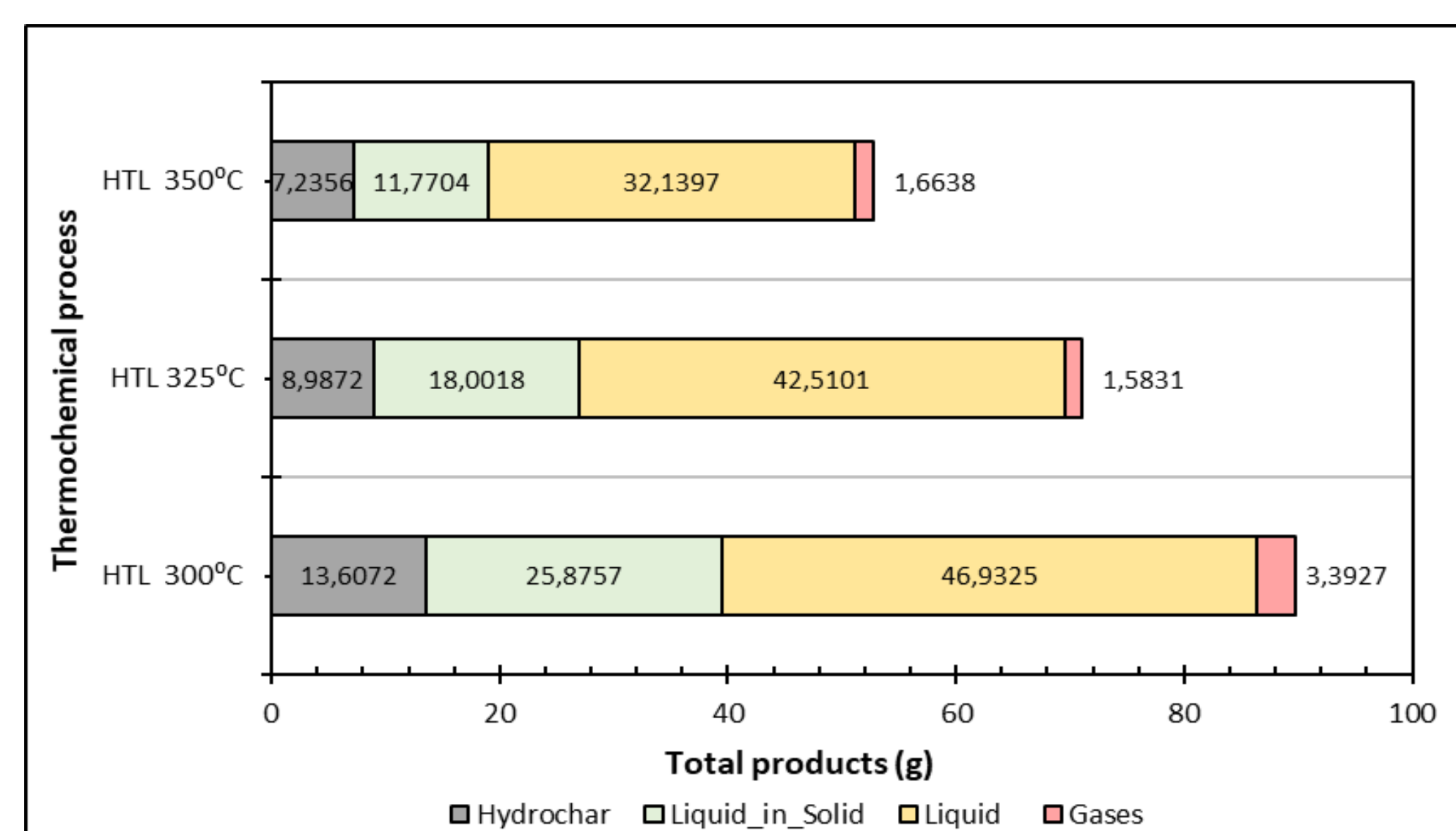


Fig 3. Product masses of hydrothermal liquefaction (HTL)

- In the hydrothermal carbonization experiments (HTC) it appears that the best quality Hydrochar is that which has been created at temperatures and pressures of 225°C in the presence of 6ml of water due to a higher value of calorific value, while the same presence of water (6ml) at a lower temperature of 200°C, although it led to the creation of more of Hydrochar percentage from all experiments of both different temperatures had a lower calorific value.
- The analysis of the total phenolic content showed the highest concentrations in the first experiment at a temperature of 200 °C thus showing the effect of water, temperature and developed -reactor-pressure on lignin. The concentration of phenols decreases linearly for both different temperatures 200 °C and 225 °C. What is observed is that there is an increase in the phenolic content in the second experiment 225 °C (8ml water) in relation to the corresponding experiment 200 °C, regardless of the fact that the COD concentration is higher in experiment 200 °C.

CONCLUSIONS

- At high temperatures and pressures, water has the ability to reduce its polarity and has characteristics similar to organic solvents and this is shown by the high concentration of COD at the hydrothermal liquefaction (HTL) temperatures.
- There is a decrease in the concentration of phenols with increasing moisture content (6ml and 10ml) in both hydrothermal carbonization experiments (HTC) 200°C and 225°C this is not the case for the pressure conditions created for the amount 8ml of moisture, where the increase in temperature from 200°C to 225°C leads to an increase in the concentration of phenolic content.