The effect of CO2 hydrothermal liquefaction on the quality of biocrude

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INTRODUCTION

The island of Lesvos has a highly developed food industry whose products are an important factor in the economic development of the island. In addition, Lesvos is known for its local alcoholic spirit, ouzo, one of the most popular alcoholic distillate in Greece. This distillates is flavored with anise and thus a large volume of anise waste arises at the end of the distillation. The widespread use of anise by the local industry produces a significant amount of waste that needs to be managed and treated. By the end of distillation, anise is a waste with a high percentage of moisture exceeding 70%. Therefore, the high moisture content of anise makes it an ideal material for hydrothermal liquefaction (HTL). Hydrothermal liquefaction is a thermochemical process that converts high-moisture organic waste into high-value liquid fuels and chemicals. HTL's main product is biocrude, a liquid fuel with similar characteristics to crude oil and a product with high heating value. Together with biocrude, chemical compounds such as aliphatic hydrocarbons, carboxylic acids, esters, aromatic and phenolic compounds are produced. The main reactions to HTL are hydrolysis, decarboxylation, dehydration, condensation and polymerization. The high temperatures developed in HTL combined with specific reactions such as decarboxylation contribute to the high calorific value of biocrude. In these thermochemical mechanisms, which contribute to the upgrading of the quality of biocrude, CO_2 plays an important role.

METHODS

HTL reactor experiments: The experiments took place at a Parr 4570A hydrothermal reactor, with a capacity of 1 L. A total of 12 hydrothermal liquefaction experiments were carried out. More specifically, three temperatures developed: 310 °C, 350 °C, 390 °C. At each temperature 4 different experiments were performed with different pressure conditions in each, with the addition of gases. The different cases were as follows: no pressure, addition of 10 bar N_2, addition of 1 bar CO_2 and 9 bar N_2, addition of 1 bar CO_2. Before the start of the experiments, the air was removed with the addition of N_2. In all experiments of hydrothermal liquefaction, the residence time was 2 h. This study focuses on the quality of biocrude and the effect that the presence of gases and specifically CO_2 had on it. The analyses carried out were pH, conductivity, COD while an important role in the conclusions was played by the analyses for VFAs and FAMEs. The determination of concentrations of VFAs and FAMEs was carried out in a Shimadzu Nexis 2030 GC-BID gas chromatograph.

GC analysis: The VFAs were measured with the Agilent J&W HP-FFAP column. The parameters of the method included 1 μL sample injection volume, an injection temperature of 160 °C, an oven temperature program ranging from 80°C to 230 °C, a flow rate of 59 ml/min and BID detector temperature at 280 °C. FAMEs were measured using the mega 10 column. In addition, the parameters of the method included 1 μl sample injection volume, an injection temperature of 240 °C, an oven temperature program ranging from 40 °C to 230 °C, a flow rate of 66,5 ml/min and BID detector temperature at 240 °C.

Sample	Description	Amount of anise (gr)	Temperature (°C)	Pressure (bar)	Residence Time (h)
S310NoP	No Pressure	200	310	100,7	2
S310N_2P	10 bar N_2 Pressure	200	310	125	2
S310N_2CO_2P	1 bar CO_2 & 9 bar N_2 Pressure	200	310	124	2
S310CO_2P	1 bar CO_2 Pressure	200	310	104,4	2
S350NoP	No Pressure	100	350	120,9	2
S350N_2P	10 bar N_2 Pressure	100	350	146,6	2
S350N_2CO_2P	1 bar CO_2 & 9 bar N_2 Pressure	100	350	147,8	2
S350CO_2P	1 bar CO_2 Pressure	100	350	128,9	2
S390NoP	No Pressure	50	390	77,2	2
S390N2P	10 bar N_2 Pressure	50	390	112,3	2
S390N2CO2P	1 bar CO_2 & 9 bar N_2 Pressure	50	390	112,2	2
S390CO2P	1 bar CO_2 Pressure	50	390	92,8	2

Table 1. Experimental conditions - HTC

Fig. 1. Image of the Parr 4570A reactor

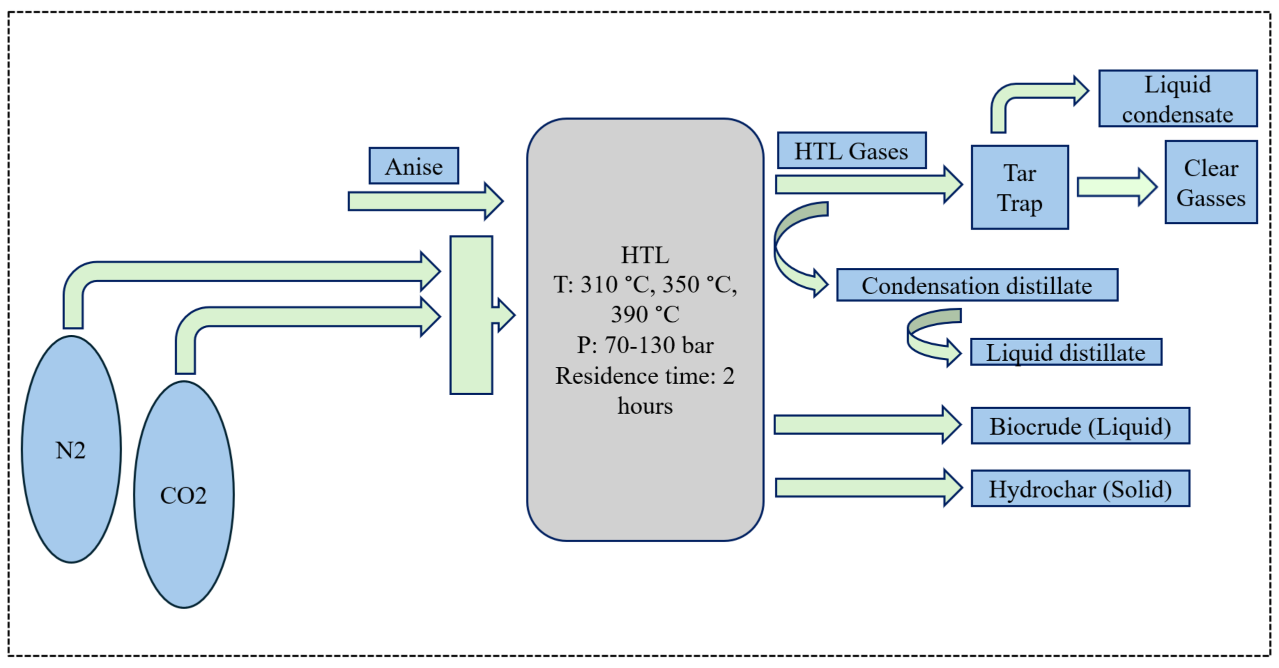

Fig. 2. Experimental scheme with sampling points

RESULTS AND DISCUSSION

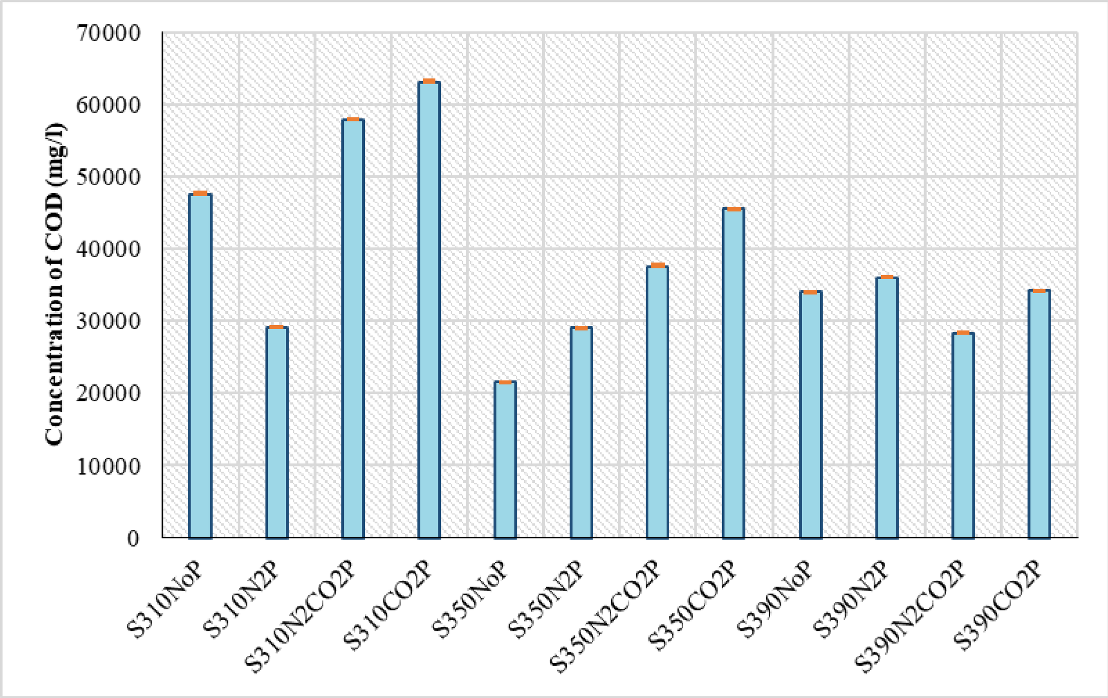

Fig. 3. Concentration of COD of HTL products

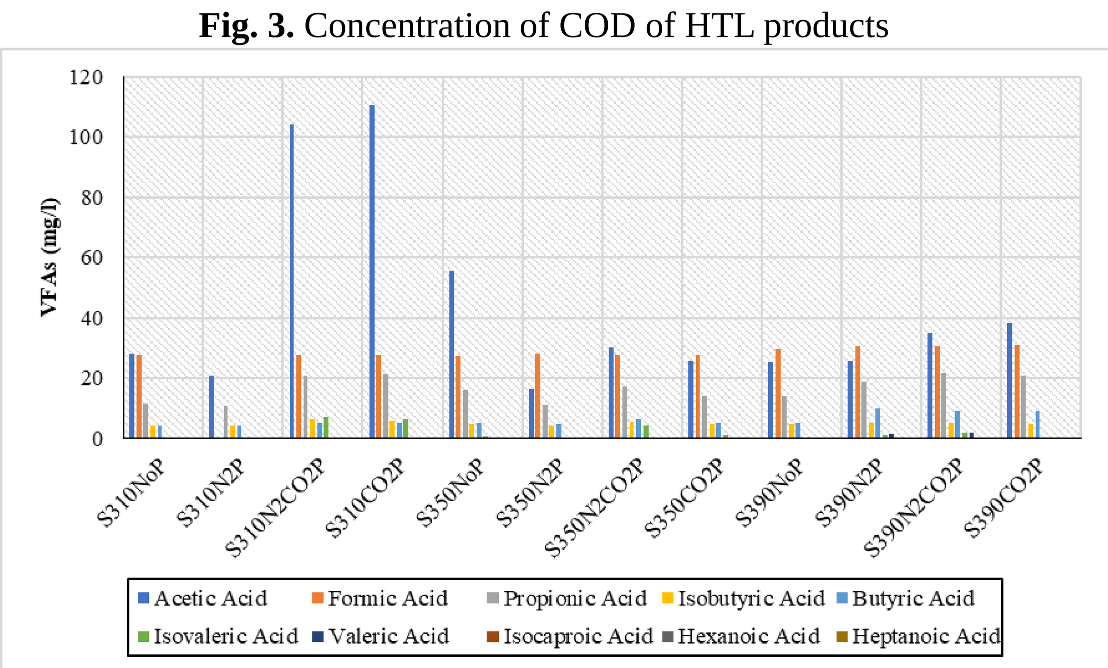

Fig. 4. VFAs concentration in liquid products of HTL

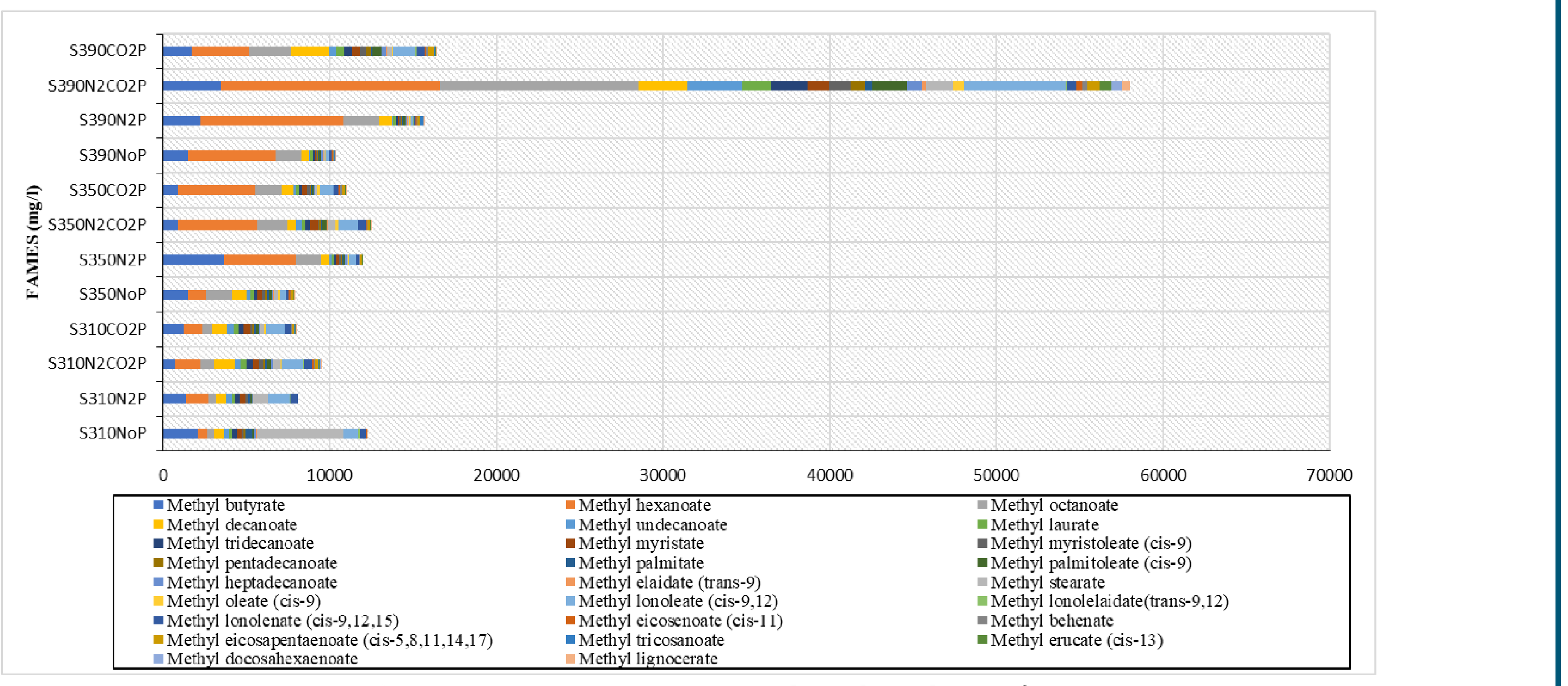

Fig. 5. FAMEs concentration in liquid products of HTL

- At all temperatures it appears that the concentration of COD shows the highest values when added the CO_2 into the reactor.
- The organic load appears to be increased in both cases of CO_2 presence.
- The highest concentrations of VFAs occur at 310 °C and specifically where experiments were carried out in the presence of CO_2.
- Across the range of temperatures, Acetic acid, Formic acid and Propionic acid appear to have the highest production.
- It is observed that at higher temperatures (350 °C, 390 °C) there are greater concentrations of FAMEs compared to VFAs.
- FAMEs show their highest concentrations in hydrothermal liquefaction experiments at 390 ℃ and specifically those added CO_2./ The FAMEs that occur in larger concentrations are as follows: Methyl Hexanoate, Methyl Octanoate, Methyl Decanoate, Methyl Undecanoate, Methyl Tridecanoate, Methyl Palmitoleate (cis-9), Methyl Linolenate (cis-9,12,15).

CONCLUSIONS

- The organic load and by extension the COD is much more increased in cases where CO_2 was added.
- Higher temperatures (350 °C, 390 °C) favor the production of longer chain carboxylic acids.
- VFAs show their highest concentrations at 310 °C.
- At all temperatures developed it is observed that the largest concentrations of VFAs and FAMEs occur in the liquid product from the experiments that took place in the presence of CO_2.
- It is observed that CO_2 affects the HTL liquid product by increasing the organic load and favoring greater production of organic chemicals (VFAs, FAMEs).
- It appears that during hydrothermal liquefaction there are thermochemical mechanisms through which the liquid fuel absorbs and traps CO_2.
- Production of liquid product rich in organic ingredients with the addition of CO_2.

References:

do Couto Fraga, A., de Almeida, M. B. B., & Sousa-Aguiar, E. F. (2021). Hydrothermal liquefaction of cellulose and lignin: a new approach on the investigation of chemical reaction networks. *Cellulose*, *28*(4), 2003-2020.

Thomsen, L. B. S., Anastasakis, K., & Biller, P. (2024). Hydrothermal liquefaction potential of wastewater treatment sludges: Effect of wastewater treatment plant and sludge nature on products distribution. Fuel, 355, 129525.