

# Unraveling HTL mechanisms of carbohydrates-proteins interactions

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## Introduction

The production of advanced biofuels from waste biomass has gained a lot of interest as possible solution to the pressing issue of global warming. Among the different technologies, hydrothermal liquefaction (HTL) has shown compelling performance for energy exploitation of organic waste. HTL is performed in aqueous environment at sub-critical temperature (250-374 °C), pressure high enough to avoid vaporization of the feed (4-25 MPa) and solid/water ratio up to 20 wt.%. The target product of HTL is an oil phase (crude) that, after upgrading, can be used as a substitute for fossil fuels. It also produces char, a gas phase rich in CO<sub>2</sub> and an aqueous phase with residual organics. The distribution among these products depends heavily on the feedstock composition (Gollakota et al., 2018). In particular, crude has shown to be increased following the trend lipids > proteins > carbohydrates (Billar & Ross, 2011). Although lipids-rich biomass would be more favorable for HTL-derived crude, it represents a high-value waste. On the other hand, proteins and carbohydrates are more abundant in organic waste. They have shown a high interaction that has been traced back to the Maillard reaction. This reaction is known to have a synergistic behavior towards crude; however, little is yet known on how this reaction affect the HTL mechanisms.

In this work, we evaluated the HTL interaction between glucose and glycine (representatives of carbohydrates and proteins, respectively) at different temperatures. The focus was directed towards the understanding of the mechanisms underlying HTL by studying interchange phenomena between the generated phases. This process was performed also through consecutive tests of the generated phases alone.

## Materials and Methods

HTL tests were conducted in a batch reactor (Parr 4575A model, 500 mL). 200 mL solution of glucose and glycine, alone or in mixture, was used as reagent. The concentration was 5 wt.% (one reagent alone) or 10 wt.% (mixture of reagent with 5 wt.% each). Reaction time was kept fixed to 1 h starting from the time the set point temperature was reached. After cooling the gas was sampled and then the reactor was opened. The liquid contained in the reactor was vacuum filtered to separate suspended char. The permeate was extracted with diethyl ether (1:1 mass ratio); the raffinate was defined as aqueous phase (AP), while the DEE of the extract phase was dehydrated and evaporated through a rotavapor (B-AP). The reactor, as well as the solid removed from the liquid, was cleaned by washing with ethyl acetate. The ethyl acetate solution was vacuum filtered. The solid removed by the filter was dried at 105 °C overnight and the resulting product constituted the char. The ethyl acetate contained in the permeate was dehydrated and evaporated through a rotavapor. The resulting product was defined as B-S and the sum between B-S and B-AP represented the crude. Consecutive tests were also performed by using the separated phases as feedstock for a second test at 350 °C for 1 hr.

Gas, aqueous phase and oil compositions were analyzed by micro-GC (SRA), HPLC (Shimadzu) and GC-MS (Agilent). Char and oil phases properties were also evaluated through TGA (Mettler Toledo) and ATR-FTIR (Burker). Mass yields were based on the dry mass of the reagents, while AP yield was defined as complement to 100%.

## Results and Discussion

In Figure 1a the mass yields for the glucose-glycine mixture are reported at different temperatures. Char showed a maximum yield at 250 °C that decreased to less than one third at 350 °C. On the other hand, crude yield showed an increasing trend with increasing temperature. These trends were different compared to product yields with glycine and glucose alone (data not shown): the former had a limited crude production whereas the latter exhibited constant solid yield over 250 °C and crude yield with maximum at 250°C. The synergistic/antagonistic behavior for the glucose-glycine mixture is shown in Figure 1b by plotting the differences between the experimental values of the glucose-glycine mixture and the averaged values of glucose/glycine reacting alone. The glucose-glycine interaction is clearly observable. Gas yield strongly exceeded the yield of the individual compounds: at 200 °C a high amount of CO<sub>2</sub> is produced, probably due to the Strecker degradation that occurs during melanoidin formation of Maillard reaction (Fang & Schmidt-Rohr, 2009). The difference in gas yield decreased as the reaction temperature increased, ending with a zero difference at 350 °C. In fact, the gas yield from glucose-glycine

remained approximately constant while the gas yield from monomers alone increased. Char and crude formations also appear to be strongly affected by the interaction, but in opposite ways: low temperature favored char yield while high temperature favored crude yield. Crude formation seems hence characterized by different mechanisms whether glucose-glycine reacted together or separately.

To deepen the relationships between the phases, a consecutive test campaign was performed (Figure 2a-b). With glucose alone at 350 °C gas clearly increased thanks to contributions from all the phases, while remained constant for glucose-glycine. Char slightly decreased with glucose, producing small organics solubilized in the AP, while glucose-glycine derived char is mostly converted into crude. Crude from glucose slightly decreased despite the contribution coming from the AP phase. On the other hand, crude from glucose-glycine largely increased thanks to the important contributions of AP (melanoidin containing) and char. In the end, in both cases char seems not to be formed from crude despite a carbonization process would be expected.

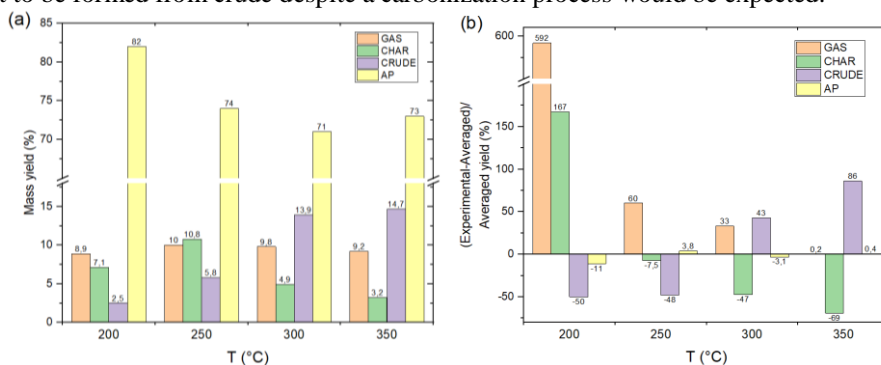


Figure 1: (a) mass yields for glucose-glycine mixture at different temperatures; (b) relative differences between experimental mass yields of glucose-glycine and mass-averaged yields for glucose and glycine alone.

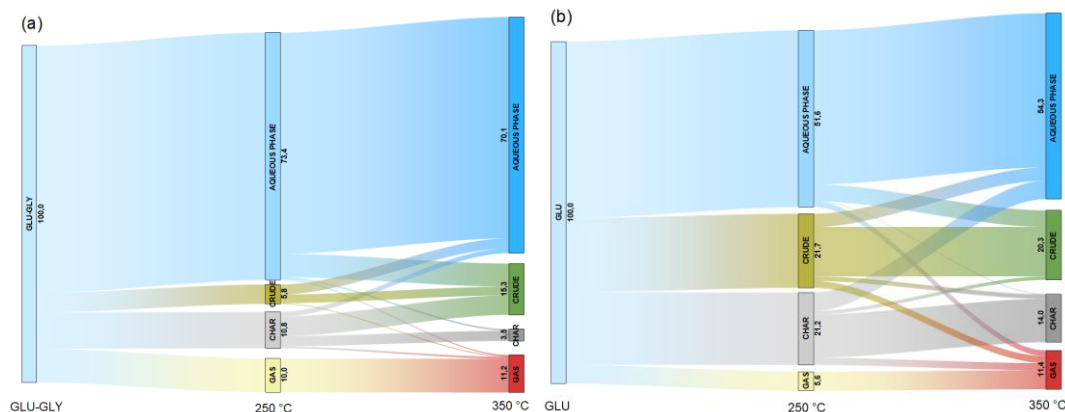


Figure 2: product distributions at 250 °C and for consecutive reactions of single phases reacting alone at 350 °C. (a) Glucose-glycine; (b) glucose.

## Conclusions

Experimental results show a strong interaction between glucose and glycine, which is observable in the variation of product distributions when they react together compared to when they react alone. In particular, the char and crude phases appear to be heavily correlated. Unlike the mechanisms that take place with glucose alone, the Maillard reaction, which occurs with the mixture, leads to a higher quantity of char at low temperature which acts as an intermediate for the crude production. This different pathway ultimately brings to a higher crude yield at higher reaction temperatures.

## References

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