Abstract

The growing energy demands led the attention on the necessity to find alternatives to fossil sources. Biomass may be one of the keys to solve this challenge, and its conversion into chemicals, fuels and energy is called biorefinery. To be sustainable from economic and environmental point of view biorefineries need to recover as much as possible of the carbon in the feedstock; however, in most of the process there is a production of a liquid side streams which contains organic compounds. For example, among the exiting processes, hydrothermal liquefaction aims to produce a biocrude, which after an upgrade step can be used as fuel. However, next to the desired product, a gas phase, a solid char and a wastewater (HTL-AP) are produced.

Aim of the thesis is testing the feasibility of the aqueous phase reforming reaction application to liquid side streams, containing diluted organics; especially the attention of this work focuses on the hydrothermal process of lignin rich feed, starting from model molecules up to pilot-plant testing looking also at environmental and economic feasibility. The water formed during the Fischer-Tropsch water was also tested to deeper understand the feasibility of APR in the various industrial frames.

Most of the works in literature focuses on simple compounds, especially alcohols and polyalcohols; however, they are not representative of a complex mixture as the HTL-AP. Starting from literature or from direct characterization of side streams, model compounds of different classes were selected and tested.

Fischer-Tropsch fraction contains small alcohols and carboxylic acids, their reactivity was assessed thanks to single compound tests and then their synthetic mixture was compared to the water produce by low temperature Fischer-Tropsch. Increase of temperature and time had beneficial effect on the conversion of the feedstock and good hydrogen productivity was obtained thanks to the presence of linear alcohols in the water. From the tests on single molecules insights into the reaction mechanism and product distribution were obtained and the importance of the hydroxyl group position was highlighted.

Then, carboxylic and bicarboxylic acids, hydroxyacids, alcohols, cycloketones and aromatics were identified as representative for HTL of lignin rich stream and tested. The tests were performed with a Pt/C catalyst and the influence of the carbon concentration (0.3–1.8 wt. C%) was investigated. Glycolic acid, acetic acid, lactic acid were mixed together and tested to understand the behaviors of single compound, with acetic acid which seems to suffer of adsorption competition on the active site. Finally residual waters from HTL of lignin were tested for the first time after a deep characterization. Deactivation of the catalyst was observed, and it was ascribed to the presence of aromatics in the water. The extent of deactivation was correlated to the reduction of surface area, which may be due to the adsorption on the catalyst of phenolic oligomers. Simple aromatics like guaiacol and phenol, were proved not to be the cause of the deactivation thanks to the use of a multi-component synthetic

mixture. Solutions to mitigate the phenomena were studied, such as active carbon adsorption and liquid-liquid extraction for the selective removal of aromatics.

Finally, the knowledge gained with batch tests were used to understand the feasibility of APR at industrial level. To do that lab scale continuous reactor was used. Indeed, the continuous mode is a necessary step to get closer to industrial application and to deeper study the stability of the catalyst.

Thanks to the characterization of the HTL water fraction synthetic mixture were prepared as close as possible and tested in continuous to study the influence of temperature and flow rate on the conversion and hydrogen production. Preliminary tests were conducted in a pilot-plant scale with the same synthetic mixture and the results were comparable with lab scale reactor.

Aqueous phase reforming can be combined with hydrothermal liquefaction to clean its water and produce a gas rich in hydrogen which can be used in the upgrading step of biocrude. A conceptual design of the HTL APR combined plant was carried out to understand the feasibility of the combination of the processes. Two cases were studied: one with lignin and one with corn stover as feedstock of HTL. Based on the plant techno-economic and environmental assessment were carried out and proved the potential of aqueous phase reforming to produce hydrogen starting from water waste. The analysis shows that the minimum selling prices for the biofuel are 1.20 for lignin rich stream and 1.17 €/kg for corn stover.