Reaction Pathway Identification Through Computer-Aided Molecular Design to Enhance Phenol Production from Bio-Oil

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1. Hydrothermal Liquefaction (HTL)

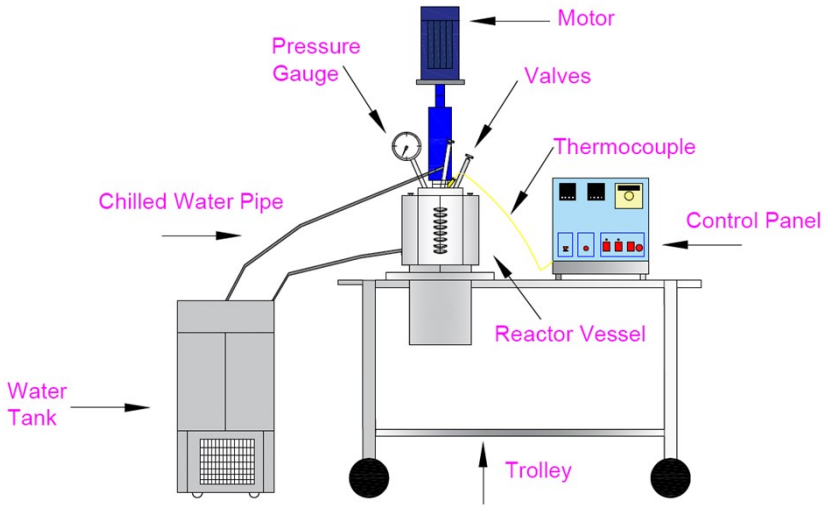

Figure S1: Schematic representation of the high pressure autoclave reactor with cooling water pump & tank system.

HTL process was carried in a high-pressure stainless-steel autoclave batch reactor with a capacity of 1L. This reactor was equipped with a rupture disc which has a burst rating of 1450 psig at 500°C for safety purpose. An autoclave consists of important parts such as cooling coil, stirrer shaft, impeller, thermowell and others, was used to close the reactor vessel. The cooling coil was used to cool down and control the temperature of autoclave by using the circulated chilled water from the auto cooling water pump & tank system. There was a motor located on top of autoclave, which provided a stirring action to the magnetic drive, and the impeller through the stirrer shaft which was threaded with magnetic drive. Moreover, a stainless thermocouple connected to the control panel was used to utilise the temperature measurement of the reactor. The thermowell in autoclave was used to house and protect the thermocouple. A pressure gauge was mounted on the reactor to measure the pressure inside the reactor vessel in bar & psi. A control panel was installed beside the reactor vessel to control the temperature and stirrer speed of the reactor.

Around 7 g of EFB and distilled water in the ratio of 1:10, 3 mL of hydrogen peroxide were fed into the reactor. Then the reactor was sealed, and the pressure indicator was observed to note down the pressure offset. Nitrogen gas line was connected to the reactor. Nitrogen gas was purged for 1 minute and the reactor pressurized to 10 bars. The reactor was inspected for leakage. Later, the motor was switched on to set stirrer rotational speed to 200 rpm. The heater was set to desired temperature and switch on. The temperature and pressure were recorded for every 3 minutes. Once the temperature inside the reactor reached its set point (275 ^{o}C), the reaction was considered starting. After 30 minutes of reaction, the heater was switched off and cooled.

After cooling of the reactor, the gas was collected by using a collection bag and analysed for carbon dioxide concentration using the carbon dioxide detector (Crowcon Gasman) for every bag of gas collected. Then, the solution was poured through a sieve into a metal container. Then, the remaining solid in the reactor was collected using a spatula to the sieve. Then, 25 ml of dichloromethane was added into the reactor to collect the remaining organic. The reactor was again extracted with distillate water for collecting the suspended solid in the reactor. After that, the solution was filtered through vacuum filter to collect solid (hydrochar). The solid collected from vacuum filter and dried in oven (Memmert UNB 500) with the temperature of 103 ^{o}C and duration of 6 hours. The solution collected in the vacuum filter flask was then poured into a separating funnel through a funnel. The organic phase was collected from the bottom of the funnel followed by the aqueous phase. DCM from the organic phase was evaporated in a rotary evaporator (Laborota 4003, Heidolph) worked at a temperature of 50˚C with a vacuum pressure of 0.085 mMPa and a rotary speed of 250 rpm for 40 min.

The organic liquid samples underwent analysis using Gas Chromatography-Mass Spectroscopy (GC-MS). Each organic sample was dissolved in methanol to ensure a uniform concentration. These diluted samples, with a concentration of 0.015 g/ml, were then introduced into the injector with injection temperature of 180 °C at a split ratio of 1:50. Separation occurred using an Elite-5ms capillary column (0.25 mm internal diameter, 30 m length) with helium serving as the carrier gas at a flow rate of 15 mL/min. The column oven initially set at 40 °C was held for 3 minutes before being ramped up at a rate of 5 °C/min to 250 °C and held for 10 minutes. The chromatogram obtained is given in Fig S2. X-axis of chromatogram represents the retention time for each compound. Retention time is the time taken for a particular compound in a liquid sample to travel through the GC column and reach the detector after injection. Compounds in liquids are separated by their retention time. The eluting compound was identified by most matching spectroscopy available in NIST library. All the major compounds in chromatogram and their area under the peak were noted. Area% of each compound was calculated from summarized area of all compounds. Quantification of phenol was conducted by injecting phenol at different concentrations into GC and plotting standardization line of chromatogram area vs concentration. Area% can give relative quantities of other chemicals.

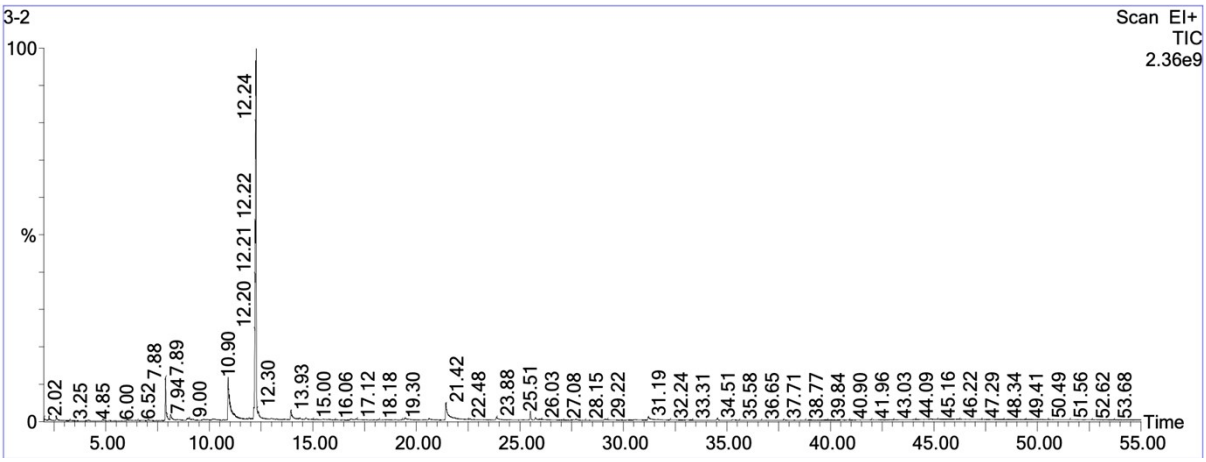

Figure S2: Chromatogram obtained from GC-MS analysis of crude bio-oil