Thermodynamic Analysis of Hydroxypropanone as Bio-Oil Model Compound to Light Hydrocarbons

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Effort to seek sustainable renewable energy has been focused since the past decades in view of the diminishing of petroleum and natural gas reserves. Bio-oil that can be obtained from biomass, has a complex, diverse, and large carbon range content in its current state, as opposed to gasoline's carbon range and lower hydrocarbon that can be used as fuel and intermediate products. Unfortunately, no specific thermodynamic study was conducted on the transformation of bio-oil into light hydrocarbon. The long and complex carbon chain of bio-oil could be cracked into smaller carbon compounds in order to make use of its abundance availability. Thermodynamic equilibrium analysis of bio-oil model compound to light hydrocarbons using overall Gibbs method of minimizing free energy was performed in this study. The composition of the equilibrium product for co-cracking of hydroxypropanone as model compound was determined in the following ranges: temperature, 300-1200 °C; HMR (hydroxypropanone/methanol ratio) and HER (hydroxypropanone/ethanol ratio), 1:12,1:6,1:3,1:1, 2:1 and pressure, 1 bar. Analysis of the feasible reactions found that main products were hydrogen, carbon monoxide, carbon dioxide, while the formation of light hydrocarbons was not spontaneous. In comparison to other products, the amount of ethylene, methane, and ethane produced was very small. HMR 2:1, at temperature 1,200 °C and pressure 1 bar and HER 2:1, at 1,200 °C and pressure 1 bar were the optimum conditions for ethylene production.

1. Introduction

With growing global population, rising living standards globally and a finite supply of fossil fuels with negative environmental consequences, the demand for clean and sustainable energy has rapidly risen. The main source of energy in the world so far is non-other than fossil fuels (Bezergianni and Dagonikou, 2015). Unfortunately, despite of its benefit, fossil fuels give countless bad effects towards the environment such as air pollution, water pollution, and others. Furthermore, the combustion and consumption of fossil fuels releases noxious greenhouse gases (Dayaratne at al., 2015). Because of that, researchers around the world enhance their research effort to seek for renewable energy alternatives.

Out of numerous available alternative fuels, bio-oil has emerged and is deemed as highly potential renewable source of fuel because of its unique properties and it can be obtained from abundantly available biomass. For instance, catalytic biomass reaction can produce high-quality bio-oil by rapid pyrolysis process (Aziz and Makkawi, 2012). Bio-oil can be utilized as a source of energy for engines (Davidovits, 2013), as well as environmentally friendly binder and organic chemical resource (Dayaratne and Gunawardana, 2015). The usage of bio-oil from biomass could minimize the greenhouse effect and the occurrence of acid rain (Che et al., 2019). Bio-oil is viscous, acidic and unstable due to the availability of its oxygenated components. On top of that, the oxygen level in bio-oil is also high. Bio-oil has a complicated chemical composition with mainly water, organics and traces of ash. Bio-oil applications are narrow due to the drawbacks of crude bio-oil, such as high humidity, acidity, high viscosity, and low heating value (García-Gómez et al., 2021). Organic acids, ketones, aldehydes, esters, phenols, furans, and anhydrous sugars are among the 300 organically active compounds found in bio-oil, which belongs to diverse functional groups. The low hydrogen-carbon ratio of crude bio-oil is an excellent molecule, which can act as a solvent for bio-oil. The greatest performance for cracking from a specific functional group in bio-oil can be observed in ketones. Hydroxypropanone is a common and dominant ketone in bio-oil that possesses five-membered rings and hydroxy groups. Ketones in

the form of hydroxypropanone derived from mango residue pyrolysis, emerged as the highest chemical yield in bio-oil (34 wt%) (Negahdar et al., 2016).

As unique as it is, bio-oil existing state can be transformed into more valuable compounds by further processing and treatment. Among the possible methods are deoxygenation and catalytic cracking processes (Valle et al., 2021). The catalytic cracking technique increases the attraction of the olefin in the absence of high hydrogen pressure, and aromatic compounds found in bio-oil, in addition to increasing coke accumulation on the catalyst (Monoj Bardalai, 2015). There are some benefits to catalytic cracking over hydro processing since no hydrogen is needed, low operating cost due to atmospheric pressure application and temperatures are close to those used in bio-oil manufacturing. By removing oxygen from the reaction in the form of CO, CO_2, and H_2O, catalytic bio-oil cracking produces hydrocarbon-rich high-grade fuel.

Catalytic cracking has been proven to transform specific compound (that is present in bio-oil) to more value added products. However, running various experimental testing for other feed and co-feed compound could be costly and time consuming. Hence, thermodynamic study is introduced and carried out to provide prediction on the formation of important products from the cracking of bio-oil model compounds. The model compounds can also be used to forecast different characteristics such as enthalpy or balance of phases for the reactions involved, state equations, coefficient of activity, empirical or system-specific specialties (Marques and Guirardello, 2018). The choice of models may depend on criteria like process species and compositions, temperature and pressure ranges, data availability, as well as other aspects. Some of the numerical models that are now considered computer models include computational fluid dynamic models, stochastic models, linear programming models, thermodynamic models, and chemical percolation models. All these models are designed for the purpose of simulating the physical flow activities, combustion, and other chemical reactions (Ma and Hanna, 1999). Various properties such as phase and enthalpy equilibrium can be predicted by using thermodynamics models.

Recently, Liang and co-workers had performed thermodynamic analysis of acetic acid as bio-oil model compound conversion to light hydrocarbon, specifically ethylene and hydrogen (Liang et al., 2021). The outcome was very promising but more work still need to be done to investigate the performance of other model compounds for this thermodynamic study. Thermodynamics is an energy concept in which important element is the temperature as it is related to the average of molecular motions (Subsadsana et al., 2017). Thermodynamic analysis is necessary to identify the process's impact parameters on the reaction and the amount of the desired and unwanted products. As far as we are concern, thermodynamic analysis of hydroxypropanone as a model compound has not been investigated yet. As one of the highest content of bio-oil, hydroxypropanone as a model compound should be investigated for its cracking conversion to light hydrocarbon and hydrogen. This will provide more understanding of the fundamental sciences required for the conversion of bio-oil to light hydrocarbon. The goal of this research is to determine the chemical equilibrium for the conversion of hydroxypropanone and methanol/ethanol as co-reactant for the production of light hydrocarbons, hydrogen and other co-products (CO_2, H_2O, CO and coke). The process was carried out by varying the parameters such as feed ratio and temperature by thermodynamic modelling. A list of possible reactions taking place and its respective Ln K versus temperature data is presented to comprehend the overall scenario.

2. Methodology

HSC Chemistry version 11 was used to conduct the thermodynamic analysis. This program uses the Gibbs energy minimization approach for equilibrium calculations. The Gibbs program looks for phase compositions in which the system's Gibbs energy can be reduced to a minimum in a specified mass balance (a constraint minimization problem), constant pressure, and constant temperature. It is worthy to note that there are no input reaction equations. The species such as hydroxypropanone ($CH_3C(O)CH_2OH$) (g), hydroxypropanone with methanol (CH_3OH) (g) and hydroxypropanone with ethanol (C_2H_5OH) (g) were considered as input species in this study. Methanol and ethanol are the co-reactant to provide source for oxygen and hydrogen. Hydrogen (H_2) (g), methane (CH_4) (g), carbon monoxide (CO)(g), carbon dioxide (CO_2) (g), steam (H_2O) (g), ethylene (C_2H_4) (g), and ethane (C_2H_6)(g), were the outlet gas products while carbon, aromatics, aliphatics, alcohols, esters, ketones, phenols and acids were other reaction products. This study did not include any other by product formation.

The co-cracking for bio-oil production was based on the following parameters: temperatures, pressure and feed ratio (hydroxypropanone to methanol ratio (HMR) & hydroxypropanone to ethanol ratio (HER)). It's critical to look into the product distribution trends for bio-oil co-cracking in relation to temperature changes, pressure, the hydroxypropanone/methanol ratio, and the hydroxypropanone/ethanol ratio. The reaction products were supposed to have a thermodynamic balance in the reactor. The total intake of 2 kmoles was fixed for hydroxypropanones, hydroxypropanone with methanol and hydroxypropanone with ethanol. The working

temperature ranged from 300 °C to 1,200 °C, and the acetic acid to alcohol ratios were 1:12, 1:6, 1:3, 1:1, and 2:1. Meanwhile, the operating pressure was set at 0.1, 1, 5, 10 and 50 bars. In all of the examples investigated, complete (100 %) conversion was observed, confirming the feasibility of the bio-oil co-cracking process and the positive output from the product. There was an acceptable error limit to the accuracy of the supplied data.

3. Results and discussion

Table 1 tabulates the list of feasible reaction for the cracking of hydroxypropanone. 20 reactions were listed which were labelled R1 to R20. The carbon formation region, optimum conditions, and the process enthalpy were also determined. It is worthy to note that the main cracking occurred via R1 (Steam reforming of hydroxypropanone) followed by R2 and R3 which is basically the thermal decomposition reaction. Figure 1 illustrates the temperature-dependent equilibrium constants for all reactions. A negative Gibbs free energy change (Gr) denotes a more realistic spontaneous reaction, according to thermodynamic principles. On the other hand, positive Gr thermodynamically limits the reaction. The equilibrium constant has an effect on the reaction's constant (K). Based on Figure 1, larger ln K is defined as spontaneous reaction where the reactions are most likely to happen.

Table 1 Feasible reaction in cracking of hydroxypropanone

No	Reaction	Type of reaction
R1	$C_3H_6O_2 + 4H_2O \rightarrow 3CO_2 + 7H_2$	Steam Reforming of hydroxyacetone
R2	$C_3H_6O_2 \rightarrow C_3H_4O + H_2O$	Thermal decomposition
R3	$C_3H_6O_2 \rightarrow CO_2 + C_2H_6$	Thermal decomposition
R4	$CH_4 \rightarrow 2H_2 + C$	The production of coke is caused by the breakdown of CH_4.
R5	$2CO \rightarrow CO_2 + C$	Coke formation by Boudouard reaction
R6	$CO + H_2O \rightarrow CO_2 + H_2$	Water gas shift reaction (WGSR)
R7	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	Methane steam reforming
R8	$CH_4 + H_2O \rightarrow CO + 3H_2$	Methane steam reforming
R9	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	Methane dry reforming
R10	$CO + 3H_2 \rightarrow CH_4 + H_2O$	Methanation reactions
R11	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Methanation reactions
R12	$2CO + 2H_2 \rightarrow CO_2 + CH_4$	Methanation reactions
R13	$C + 2H_2 \rightarrow CH_4$	Hydrogenation or methanation reactions
R14	$CO + H_2 \rightarrow C + H_2O$	Carbon monoxide reduction reaction
R15	$CO_2 + 2H_2 \rightarrow CO + 2H_2O$	Reverse water gas shift reaction (RWGSR)
R16	$CO_2 + H_2 \rightarrow CO + H_2O$	Coke gasification
R17	$C + H_2O \rightarrow CO + H_2$	Coke gasification
R18	$CaO + CO_2 \rightarrow CaCO_3$	Coke gasification
R19	$CaO + H_2O \rightarrow Ca(OH)_2$	Coke gasification
R20	$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$	Coke gasification

Based on Figure 1, it can be seen that reaction for coke gasification (R18, R19, and R20) are strongly spontaneous reactions at any temperature within the studied parameter. Reverse water gas shift reaction (RWGSR) (R15) is limited within the whole investigated temperature. Reactions R2, R3, R4, R7, R8, R9, R14 and R17 are exothermic and likely to occur at lower temperature which is below than 600 °C due to its ln K positive magnitude. These reactions are restricted at the high temperature (>600 °C) due to their negative ln K and equilibrium limitation.

The large negative values of ln K for R1 indicate that these reactions are not feasible to occur except at very high temperatures. R5, R13 and R15 can only occur at high temperature (>700 °C). Below that temperature, the reaction will be affected by equilibrium limitations. Meanwhile for R6, this reaction is possible at above 900 °C for formation carbon dioxide and hydrogen but these products also might be produced at lower temperature which is 700 °C at R5 and R12. Formation of methane from R10 and R11 will only occur at high temperature (700 °C).

Figure 2 illustrates the effect of HMR and HER on the production of hydrogen through co-cracking of hydroxypropanone with varying temperatures set at a pressure of one bar. From Figure 2a, it can be identified that hydrogen production steadily increased with temperature, and hydrogen production started to be stagnant when it reached its peak after 1,000 °C. HMR 1:6 emerged as the best ratio for hydrogen production, just a bit

lower than if hydroxypropanone was solely cracked. Figure 2d showed the influence of HER on the production of hydrogen at a 1 bar pressure at different process temperatures. Generally, hydrogen production increases steadily with the temperature and starts saturating and slightly increasing after the peak reaches its maximum. There are only slight differences between each HER ratios. The increase of hydrogen initially was mainly triggered from R1. Reactions R4, R7, R8, R9 and R17 although produces hydrogen, it was unlikely to take place at a lower temperature. However, upon comparing between the effect of methanol and ethanol co-feeding, methanol co-feeding showed more attractive hydrogen production amount, with the same trend. Should the purpose of cracking is solely for hydrogen formation, hydroxypropanone cracking without co-reactant is preferable.
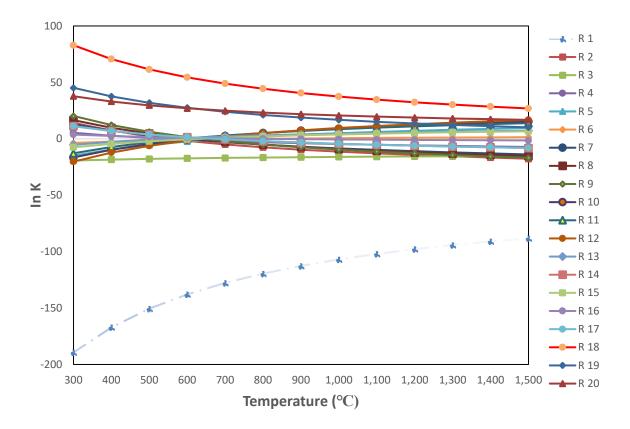

Figure 1: Co-cracking of hydroxypropanone involving equilibrium constants of reactions at atmospheric pressure.

Figure 2b shows the trend of carbon monoxide moles that were produced from hydroxypropanone co-cracking with methanol at 1 bar pressure. It was observed that in all cases, the yield of carbon monoxide increased with temperature, similar to the trend of hydrogen formation. The carbon monoxide yields also increased with rising HMR at constant pressure. For example, carbon monoxide was low at lower HMR (HMR = 1:12) but as temperature increased, CO progressively increased as well. The unpredictable nature of high temperatures carbon monoxide can be linked to the balance between water gas shift reaction (WGSR)(R6) and R15 reverse water gas shift reaction (RWGSR). However, the low amount of carbon is related to the RWGSR reaction (R15).

The methanation process is responsible for the low amount of carbon monoxide at high temperatures (600 °C) (R10 and R12) that actively consumes carbon monoxide. Figure 2e showed carbon monoxide moles formation with temperature when hydroxypropanone is co-cracked with ethanol (HER) at 1 bar pressure. The carbon monoxide output increased in all situations with temperature, showing similar trend to that of Figure 2b. Carbon monoxide production increases with HER at constant pressure. At lower HER (HER = 1:12) carbon monoxide was low but increased steadily with temperature. The spontaneity of carbon monoxide at high temperature can be related to the RWGSR reaction (R15). However, the least amount of carbon monoxide at temperature below 700 °C could be allocated to the R8, R9 and R17.

By referring Figure 2c, the number of ethylene, which is represent light hydrocarbon, is produced at varying temperatures and HMR at 1 bar pressure. From the observation of graph, moles of ethylene began to increase at temperature around 800 °C. Similarly, Figure 2f illustrates the number of ethylene moles production at higher temperatures and HER at 1 bar pressure. It can be discovered that moles of ethylene start to rise at 800 °C and increasing at higher temperature around 1,200 °C. The HER did not have much effect on the production of ethylene. The 3 main reactions that initially triggers the formation of light hydrocarbon are R10, R11 and R13. Methane is formed in all these reactions and at higher temperature methane dissociate to unstable methyl radical. One unstable methyl radical combines with another methyl radical and forms ethane.
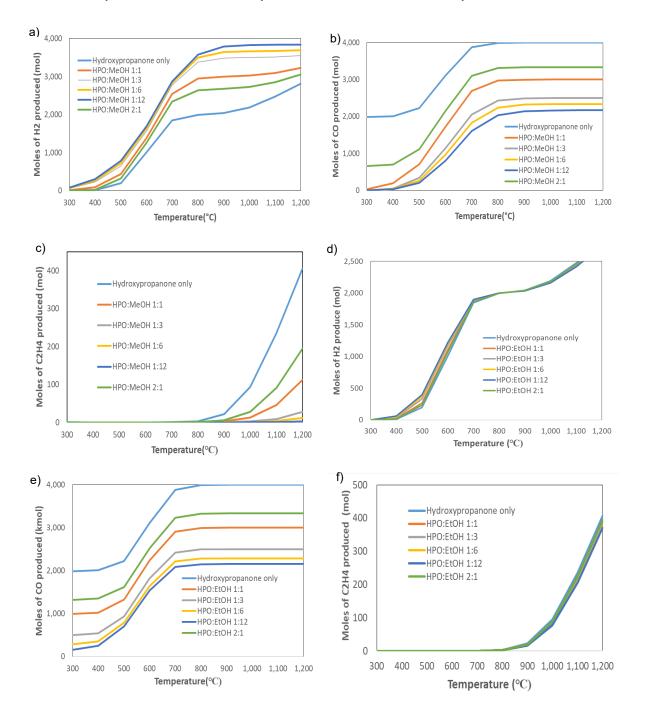

Figure 2: Production yield: (a) H_2, (b) CO and (c) C_2H_4 for various HMR at 1 bar and (d) H_2, (e) CO and (f) C_2H_4 for various HER at 1 bar

Higher temperature induces ethane to release hydrogen and further form ethylene. These steps and the high temperature above 900 °C explain the reason ethylene formation commences at high temperature.

4. Conclusion

In order to map the effect of HMR and HER on product dispersal patterns at pressure 1 bar and 300 °C to 1,200 °C temperature within for ethylene yield, thermodynamic analysis of the hydroxypropanone co-cracking process was performed. To observe its impact on product yield, the effect of varying pressure was also carried out. Calculations of thermodynamic equilibrium show favorable yields for production of hydrogen and syngas, but not ethylene. The ideal situation for hydroxypropanone at temperature 1,200 °C and pressure at 1 bar with HMR 2:1, ethylene production can be increased utilizing methanol as a raw material. The optimum condition for maximizing the production of ethylene for hydroxypropapone with ethanol as raw material was 1,200 °C and 1 bar with HER 2:1. The production of light hydrocarbons in the presence of suitable catalysts can significantly improve by comparing the present study to numerous experimental works. Acceptable hydroxypropanone and selective catalysts are needed to promote light hydrocarbon production and to limit coking in optimal reaction conditions.

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