

Thermodynamic Analysis of Ethyl Acetate as Bio-Oil Compound to Light Hydrocarbons

Shalini Velayuthem, Mahadhir Mohamed, Mazura Jusoh, Zaki Yamani Zakaria*

School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310, Skudai, Johor
 zakiyamani@utm.my

Increasing energy demand, world has generated significant interest in using renewable, sustainable and environmental friendly fuels simultaneously diminishing fossil fuels concerns that are known to deplete in future and lead to environmental issues. Renewable energy is taking path for sure to replace fossil fuels. Bio oil is considered to be potential candidate which obtain from various renewable resources. Bio oils are very complex mixtures of short and long chain oxygenated compounds. In order to make use of the available bio-oil, the relatively longer carbon chain of bio-oil will be cracked to smaller carbon compounds. Equilibrium thermodynamic analysis of light olefins production from bio-oil model compound has been recently conducted using total Gibbs free energy minimization technique. The co-cracking of ethyl acetate as bio-oil model compound has not been studied for the light hydrocarbon production. The following parameter range was used to compute the thermodynamic equilibrium compositions for co-cracking of ethyl acetate: temperature (300 - 1,200 °C); ethyl acetate/methanol ratio (EAMR) and ethyl acetate/ethanol ratio (EAER) of 1:12, 1:6, 1:3, 1:1, 2:1 and pressure (1 bar). Hydrogen, carbon monoxide, carbon dioxide and coke are among the products that are formed alongside the light hydrocarbon through literature review. According to equilibrium studies, ethylene production is low in proportion to syngas such as hydrogen and carbon monoxide. Nevertheless, optimum conditions for the production of ethylene are EAMR ratio 2:1, at 1,200 °C and 1 bar, and EAER ratio 2:1, at 1,200 °C and 1 bar.

1. Introduction

Over centuries, energy generated through burning of fossil fuels are required to propel our vehicles, produce and provide electricity to our homes and power the manufacturing industries. Gani (2021) states, that fossil energy is the primary source in the world. Energy sources can be characterized as renewable and non-renewable energy. Renewable energy sources refer to clean energy that comes from natural processes and source that can be replaced in time and will not run out for decades. Non-renewable energy sources, in the other hand, will not be replenished and eventually run out. Fossil fuel such as oil, natural gas and coal are common resource of non-renewable energy. These resources are physically and economically limited (Capellán-Pérez et al., 2014). Baz et al. (2021) states, that high consumption of energy results in high levels of carbon emission especially from fossil fuel resources. Combustion of coal generates two times more carbon dioxide than combustion of natural gas according to Paraschiv and Paraschiv (2020). In view of the increasing energy demand, the world has aroused considerable interest in renewable, sustainable usage and environmental friendly fuels. The emergence of renewable fuels simultaneously ease the diminishing fossil fuels concern that are known to deplete in future and also eradicate the environmental issues triggered. More studies and researches are being ongoing for the development of renewable energy.

Biofuel such as biogasoline is one such promising candidate for the replacement of fossil fuels which reduce greenhouse gas (GHG) emissions and maintain a sustainable environment (Sharma et al., 2020). It has been stated that biofuels are categorised as first, second and third generation (EdwinGeo et al., 2021). First generation refers to biodiesel, bio alcohols, bio gas, vegetable oil and syngas manufactured from various feedstock such as starch sugarcane by-product, plant oil and animal fatty acids. Grasses, plant, seeds and trees are some of the sources for secondary generation and algae based oil as third generation of biofuels. Sumathi

et al. (2008) states that biodiesel is safe, non-toxic, biodegradable and produce less air pollution than petroleum based diesel (petro-diesel).

However, it would not be adequate to depend on biodiesel and biogasoline to fulfill the great global energy needs. Clean fuel or bio-oil can be the answer to supplement the energy demand. Bio-oil can be obtained from endless biomass supply around us and can be regarded as nature's abundant resources. Fast pyrolysis process of biomass increases the yield of bio-oil. Zhang et al. (2021) states that bio-oil is a complex chemical compound comprising lightweight or heavy oxygenated compounds such as ketones, aldehydes and carboxylic acids. Bio oil has drawbacks such as high oxygen and water content, high viscosity, high acidity and thermal instability (Valle et al., 2021). A crude bio-oil model compound is chosen for catalytic cracking to convert it into light hydrocarbons by removing carbon monoxide, carbon dioxide, and water as unwanted by-products (Chen et al., 2018). Many researches were carried out to obtain a high yield of target products and minimum composition of coke by optimizing catalysts and operating conditions. Methanol and ethanol serve as solvents that could be added to crude bio-oil to maximize the hydrocarbon yield and minimize the coke formation.

The study hypothesis is that light hydrocarbon (which in this case represented by ethylene) can be produced from bio-oil (represented by ethyl acetate). In order to achieve this hypothesis, experimental work could be conducted but it may lead to higher cost and consume more time and energy. Thermodynamic analysis is the optimal method for conducting swift investigation which avoids and eliminates all of the disadvantages associated with substantial experimental effort. Many thermodynamic studies have been reported, for example, thermodynamic analysis of steam reforming of propionic acid as bio oil model compound to produce syngas (hydrogen and carbon monoxide), carbon dioxide and methane as desired products and carbon (coke) as an undesired product at temperature (500 - 900 °C); pressure (1 - 10 bar), and H₂O/HPAc ratio (0 - 4 mol/mol) (Sahebdehfar, 2017) and thermodynamic study palm empty fruit bunches (PEFB) steam reforming derived bio-oil to produce low carbon hydrogen production (Spragg et al., 2018). Liang et al., (2021) used acetic acid and as model compound together with methanol/ethanol co-reactant to represent bio oil to produce light hydrocarbon as well. To the best of our knowledge, no thermodynamic analysis has been made to study the co-cracking of ethyl acetate to light hydrocarbon. The objective of this research is to conduct a thermodynamic analysis of the equilibrium reactions between ethyl acetate and solvents (methanol and ethanol) to generate light hydrocarbon, which in this case represented by ethylene via the minimization of total Gibbs energy method. Co-products of the reaction such as hydrogen, carbon monoxide and coke were also assessed.

2. Methodology

HSC Chemistry software Version 11 was used to simulate the thermodynamic analysis of the production of light hydrocarbon from bio-oil model compound, which in this case is ethyl acetate. HSC Chemistry software calculates the equilibrium composition of all possible combination of reactions that are able to involve in the thermodynamic system. Minimization of the Gibbs free energy technique is the main feature used to solve the equilibriums of chemical reactions involved for the analysis of the systems in the software. The feedstock species considered were (i) ethyl acetate with methanol and (ii) ethyl acetate with ethanol. Methanol and ethanol were selected as co-reactant to provide additional carbon, hydrogen and oxygen for the reaction. The process produced ethylene, hydrogen, carbon monoxide, and coke as byproducts. Ethylene is the sole considered light hydrocarbon representative, with other light hydrocarbons excluded because preliminary investigation found that other light hydrocarbon formation is too small. For example, production of allene (1.57×10^{-19} - 8.18×10^{-13} mol), propane (4.91×10^{-9} - 2.29×10^{-8} mol) and propene (1.1×10^{-11} - 8.67×10^{-8} mol). The total reactant input was set at 2 kmol. During the thermodynamic simulation work the reaction temperature was varied in the range of 300 - 1,200 °C at 1 bar. EAMR (ethyl acetate/methanol ratio) and EAER (ethyl acetate/ethanol ratio) were 1:12, 1:6, 1:3, 1:1 and 2:1. This range of parameter were considered based on previous report (Liang et al., 2021). Thermodynamic study reveals the feasibility of co-cracking of ethyl acetate where the bio-oil model compound manages to reach 100 % conversion in all instances and a yielded promising in product trends.

3. Results and analysis

Reaction mechanism or pathway for ethyl acetate and methanol/ethanol cracking to its respective products has been postulated. The process involved multiple parallel and complex reaction combinations such as decomposition, methanation, oxygenation and others as shown in Table 1 (Chen et al., 2018). For all reactions involved, the heat of enthalpy was determined to fully comprehend the scenario by utilizing species data from Yaws CL (2018). Figure 1 shows the temperature dependence of the equilibrium constants for all of the reactions mentioned in Table 1. When the reaction results into larger $\ln K$ value, it will indicate that the reaction is spontaneous as the Gibbs free energy change (ΔG_r) is negative. When ΔG_r is positive, the reaction is limited

thermodynamically (Zakaria et al., 2014). The equilibrium constant (K) determined the extent to which the reaction occurs.

Table 1: Possible reactions of co-cracking of ethyl acetate

R	Type of reaction	Chemical reaction equation	ΔH (kJ/mol)
1	Thermal decomposition	$\text{CH}_3\text{COOC}_2\text{H}_5 \leftrightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_4$	+65.81
2	Thermal decomposition	$\text{CH}_3\text{COOC}_2\text{H}_5 \leftrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2\text{CO}$	+163.43
3	Steam reforming	$\text{CH}_3\text{COOC}_2\text{H}_5 + 6\text{H}_2\text{O} \leftrightarrow 4\text{CO}_2 + 10\text{H}_2$	+322.20
4	Water gas shift reaction	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$	-41.14
5	Methanation	$\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$	-206.10
6	Methanation	$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-165.10
7	Methanation	$2\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_4 + \text{CO}_2$	-247.30
8	Oxidative coupling of methane	$4\text{CH}_4 + \text{O}_2 \leftrightarrow 2\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	-87.80
9	Oxidative coupling of methane	$2\text{CH}_4 + \text{O}_2 \leftrightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	-140.40
10	Ethylene dimerization	$2\text{C}_2\text{H}_4 \leftrightarrow \text{C}_4\text{H}_8$	-105.20
11	Dehydrogenation of ethane	$\text{C}_2\text{H}_6 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2$	+136.33
12	Methane decomposition	$\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}$	+74.52
13	Disproportionation	$2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$	-172.44
14	Hydrogenation of carbon dioxide	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{C}$	-90.16
15	Hydrogenation of carbon monoxide	$\text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C}$	-131.30
16	Ketonization	$\text{CH}_3\text{COOH} \leftrightarrow \text{CH}_2\text{CO} + \text{H}_2\text{O}$	+144.40
17	Ketene decomposition	$2\text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_4 + 2\text{CO}$	-76.90
18	Allene formation	$2\text{CH}_2\text{CO} \rightarrow \text{C}_3\text{H}_4 + \text{CO}_2$	-110.70
19	Hydrocarboxylation of ethylene	$\text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$	-171.59

Based on Figure 1, the thermal decomposition reactions (R1 and R2) and steam reforming of ethyl acetate reaction (R3) are highly spontaneous reactions that occur at any temperature within the specified parameter range. The water gas shift (R4) reaction is restricted to the whole temperature range. The methanation reactions (R5, R6 and R7) are exothermic, which most probably takes place at lower temperatures (<600 °C) due to a positive magnitude of $\ln K$. Due to their negative magnitude of $\ln K$ and equilibrium constraints, the methanation processes are limited to high temperatures (>600 °C)

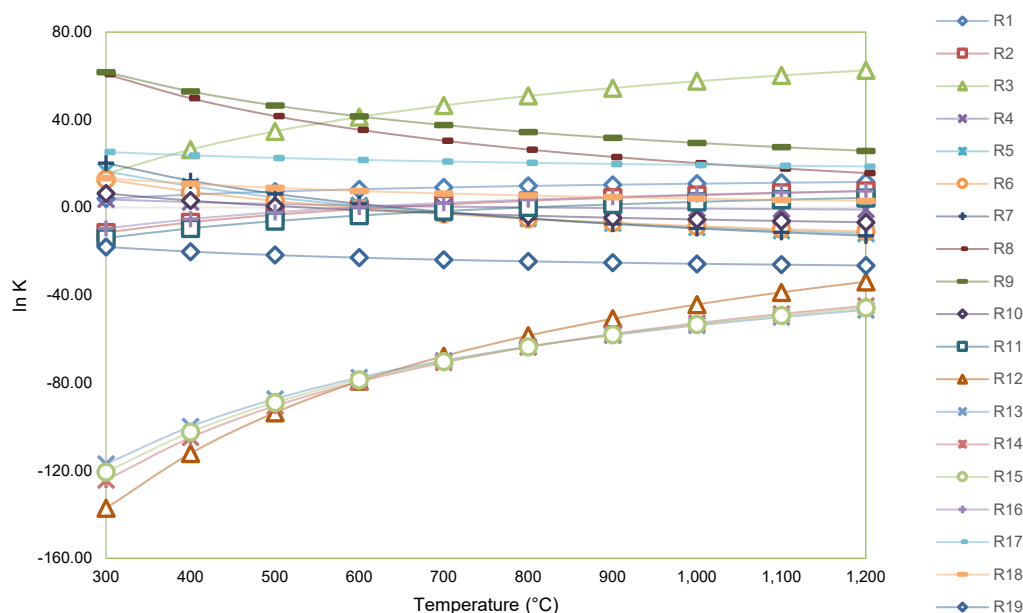


Figure 1: Temperature dependence of the equilibrium constant for co-cracking of ethyl acetate reaction at atmospheric pressure

The natural logarithm of the equilibrium constant values for oxidative coupling of methane reactions (R8 and R9) drop as temperature rises, indicating that these reactions are not possible at high temperatures. The

reaction of dehydrogenation of ethane (R11) is effective at temperature (>800 °C). At temperature (<800 °C) the reaction is affected by equilibrium limitations. Carbon is more likely form at lower temperature for R13, R14 and R15. Formation of ketene (R16) from acetic acid will only occur at high temperature and restricted at low temperature due to equilibrium limitations. Ketene then undergoes ketene decomposition (R17) and allene formation (R18). The hydrocarboxylation of ethylene is an unfavourable reaction within the studied period.

Figure 2a and 3a shows the variation in hydrogen yield at specified operating temperatures range and 1 bar with change the of EAMR and EAER ratios. Hydrogen yield was found to rise gradually with temperature. Lowest EAMR and EAER results in highest yield of hydrogen. EAMR generated more hydrogen than EAER due to the fact that ethanol solvent contributed to some hydrogen gas due to its ability to supply more hydrogen atoms. The increase in hydrogen production was triggered by the third reaction (R3). Hydrogen was not absorbed by methanation reactions (R5, R6 and R7) since they only possible at low temperature. The quantity of carbon monoxide rose gradually until a specific threshold was reached, and then stayed constant from 615 °C for both EAMR and EAER. The water gas shift reaction elucidates this situation (R4).

The carbon monoxide production from EAMR and EAER co-cracking at 1 bar and the different temperature range are shown in Figure 2b and 3b. Methanation reactions (R5, R6 and R7) and disproportionation reaction (R13) rigorously consume carbon monoxide which lead the unchanged yield of carbon monoxide at temperature >615 °C.

The amount of ethylene generated as a result of the action of EAMR and EAER at various temperatures at 1 bar is shown in Figure 2c and 3c. Maximum yield of ethylene was obtained for both EAMR and EAER of 2:1 at 1,200 °C but EAER yield higher amount of ethylene, 0.76 kmol compared to EAMR, 0.558 kmol of ethylene.

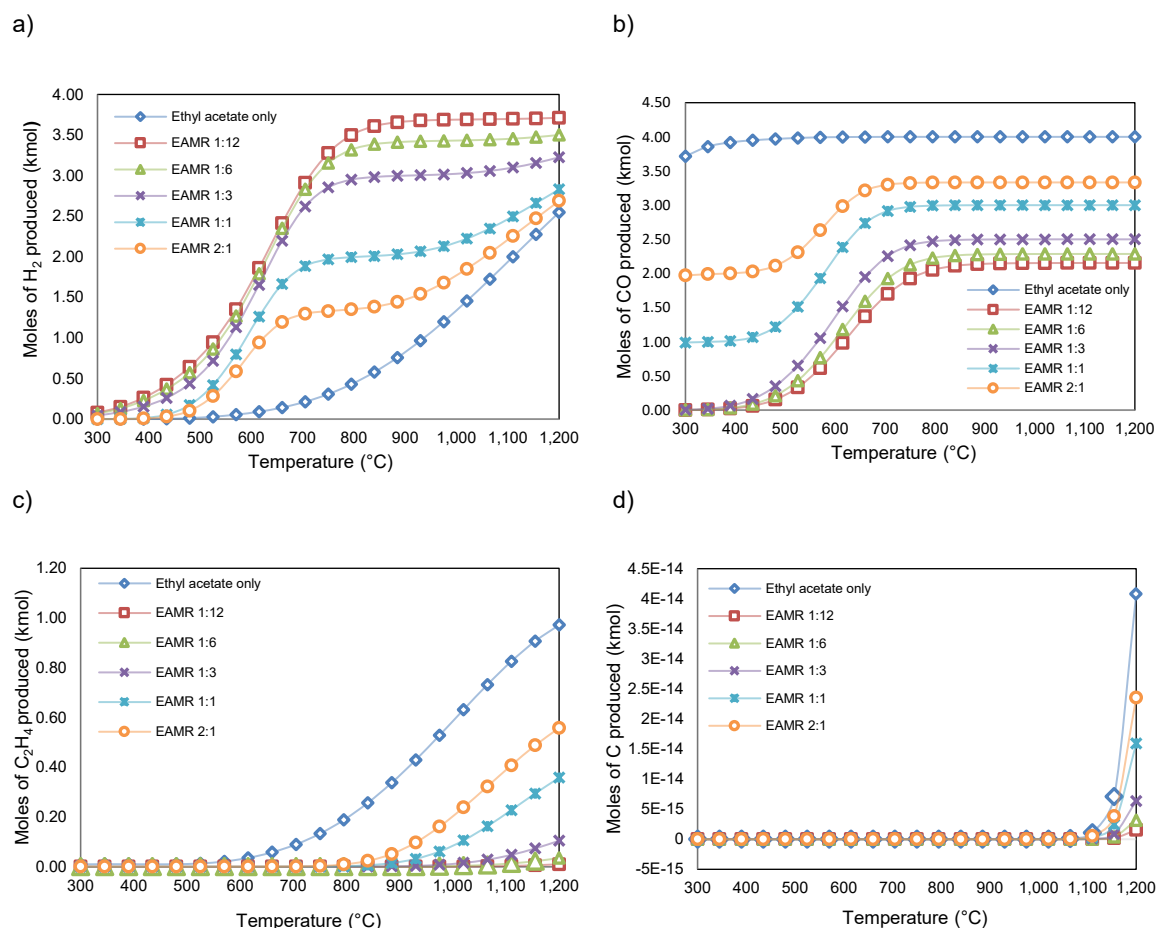


Figure 2: Yield of (a) H_2 (b) CO (c) C_2H_4 and (d) C for different EAMR at 1 bar

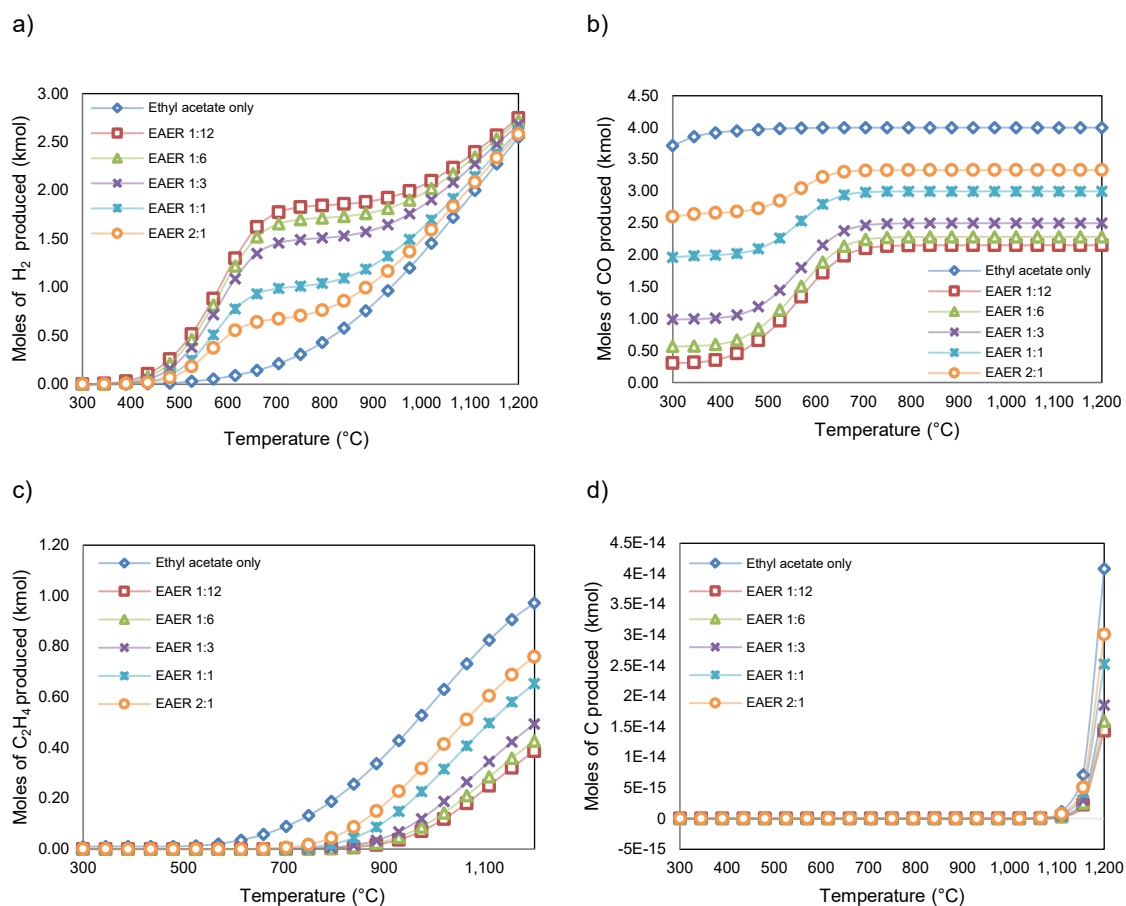


Figure 3: Yield of (a) H₂, (b) CO, (c) C₂H₄, and (d) C for different EAER at 1 bar

As a result, ethylene production was significantly increased when ethane (R11) was dehydrogenated, as opposed to oxidative coupling of methane (R9), which was more limited by equilibrium constraints. The generation of ethylene grew gradually on a thermodynamic basis, based on R10. Another alternative of direct conversion to light hydrocarbon (ethylene and ethane) is oxidative dehydrogenation which is also known as oxidative coupling of methane (R8 and R9). Methane reacts with oxidant (oxygen or carbon dioxide) at lower temperature and produce C₂ products. Methanol and ethanol solvent contribute to light hydrocarbon production in the process by enhancing the properties of ethyl acetate. Coke is an undesired product, which is regarded as problem of the choke point in the co-cracking of the ethyl acetate reaction. It inhibits the other light hydrocarbon production. Figure 2d and 3d shows the coke formation at 1 bar and designated temperature range with different EAER and EAER. The amount of coke formed was almost zero (<1,100 °C) and began to increase (>1,100 °C). The lowest amount of coke formed for EAER compared to EAER with slightly more amount. It is due to reaction of ethanol contribute to carbon formation. Liang et al. (2021) states that high EAER (acetic acid/ methanol ratio) and low EAER (acetic acid/ethanol ratio) contribute significant carbon yield.

R12, R13, R14 and R15 displays coke formation yield. Considering that the equilibrium constants of the reactions are very minimal, the processing parameters could relatively favour to influence these reactions. The disproportionation reaction represented by R13, commonly known as the Boudard reaction, may appear to be significant contributor of large chunk of coke formation. The carbon dioxide formation enthalpy is larger than carbon monoxide, although entropy generation is an integral part of this process. Carbon dioxide total free energy change of formation by oxidation is almost constant disregarding the temperature. This indicates that if catalyst is employed, it may easily be poisoned at lower temperatures, because the balance supports the production of exothermic carbon dioxide and coke. The generation of R12, R14 and R15 coke is mostly unfeasible because the reactions are negatively influenced by the equilibrium limitation. In overall, the thermodynamic analysis supported by the complex reaction discussion provided better comprehension to design the cracking reaction of bio-oil model compound. At its present state, ethylene formation seems to be the most

compared to other light hydrocarbon which appears to be too small. Ethanol as a co-reactant boosted the formation of ethylene, but it looks like if ethylene is the main target, it is better of to have ethyl acetate only for the cracking process.

4. Conclusions

It was discovered that the yield of ethylene synthesis was not promising via thermodynamic modelling and equilibrium analysis, but quite impressive for hydrogen and syngas. EAMR of 2:1 at $T = 1,200\text{ }^{\circ}\text{C}$ and $P = 1\text{ bar}$ was the optimum condition for ethylene production when methanol and ethyl acetate were considered as the feedstock. The optimal conditions for ethyl acetate and ethanol were found to be at $T = 1,200\text{ }^{\circ}\text{C}$ and $P = 1\text{ bar}$ with EAER 2:1. The findings provide valuable information on the best performing process parameters for ethylene formation. It is significant for the study of bio-oil upgrading to hydrocarbon which is more precious.

Acknowledgements

The authors would like to thank Universiti Teknologi Malaysia's UTMFr Grant (20H92) and Ministry of Higher Education Malaysia-Fundamental Research Grant Scheme (FRGS/1/2020/TK0/UTM/02/97) for financial support.

References

- Arjah A., Al-Baharab M., Li C., Arthur A., Garforth A.A., 2017, Selective cracking of light olefins to ethene and propene. *Chemical Engineering Transaction*, 57, 883-888.
- Baz K., Cheng J., Xu D., Abbas K., Ali I., Ali H., Fang C., 2021, Asymmetric impact of fossil fuel and renewable energy consumption on economic growth: A nonlinear technique, *Energy*, 226, 120357-120368.
- Capellán-Pérez I., Mediavilla M., De Castro C., Carpintero Ó., Miguel L.J., 2014, Fossil fuel depletion and socio-economic scenarios: An integrated approach, *Energy*, 77, 641-666.
- Chen G., Zhang R., Ma W., Liu B., LiLi X., Yan B., Cheng Z., Wang T., 2018, Catalytic cracking of model compounds of bio-oil over HZSM-5 and the catalyst deactivation: *Science of The Total Environment*, 631-632, 1611-1622.
- Edwin G.V., Fol G., Aloui F., Thiyagarajan S., Jerome S.M., Sonthalia A., Brindhadevi K., Saravanan C.G., 2021, Experimental analysis to reduce CO₂ and other emissions of CRDI CI engine using low viscous biofuels, *Fuel*, 283, 118829-118840.
- Gani A., 2021, Fossil fuel energy and environmental performance in an extended STIRPAT model, *Journal of Cleaner Production*, 297, 126526-126532.
- Liang L.J., Mohamed M., Ngadi N., Jusoh M., Zakaria Z.Y., 2021, Thermodynamic analysis of light hydrocarbon production from bio-oil model compound through co-cracking, In Zaini A.A., Jusoh M., Othman N., 3rd International Conference on Separation Technology, 15th August 2020, Johor Bahru, Johor, 165-174.
- Paraschiv S., Paraschiv L.S., 2020, Trends of carbon dioxide (CO₂) emissions from fossil fuels combustion (coal, gas and oil) in the EU member states from 1960 to 2018, *Energy Reports*, 6, 237-242.
- Sahebdeifar S., 2017, Steam reforming of propionic acid: Thermodynamic analysis of a model compound for hydrogen production from bio-oil, *International Journal of Hydrogen Energy*, 42(26), 16386-16395.
- Yaws C.L., 2018, *The Yaws Handbook of Thermodynamic Properties for Hydrocarbon and Chemicals*. Elsevier Science, Gulf Professional Publishing, Oxford, UK.
- Sharma A., Singh G., Arya S.K., 2020, Biofuel from rice straw, *Journal of Cleaner Production*, 277, 124101-124111.
- Spragg J., Mahmud T., Dupont V., 2018, Hydrogen production from bio-oil: A thermodynamic analysis of sorption-enhanced chemical looping steam reforming, *International Journal of Hydrogen Energy*, 43(49), 22032-22045.
- Sumathi S., Chai S.P., Mohamed A.R., 2008, Utilization of oil palm as a source of renewable energy in Malaysia, *Renewable and Sustainable Energy Reviews* 12(9), 2404-2421.
- Valle B., Bilbao J., Aguayo A., Gayubo A., 2021, Product distribution and deactivation of Y-zeolite based catalyst in the catalytic cracking of biomass pyrolysis oil, *Chemical Engineering Transactions*, 86, 865-870.
- Zakaria Z.Y., Amin N.A.S., Linnekoski J., 2014, Thermodynamic analysis of glycerol conversion to olefins, *Energy Procedia*, 61, 2489-2492.
- Zhang L., Hu X., Li C., Zhang S., Wang Y., Esmaeili V., Gholizadeh M., 2021, Fates of heavy organics of bio-oil in hydrotreatment: The key challenge in the way from biomass to biofuel, *Science of the Total Environment*, 778, 146321-146329.