

# Study of Catalytic Upgrading of Biomass Tars using Indonesian Iron Ore

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# Study of Catalytic Upgrading of Biomass Tars using Indonesian Iron Ore

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**Abstract.** Catalytic decomposition is a promising way for chemical upgrading process of low quality oil such as biomass tars. In this experiment, catalytic decomposition of biomass tars was performed over Indonesian low grade iron ore catalyst. This process is carried out in a fixed bed reactor which is equipped with preheater to convert the tars into vapor form. The reaction was studied at the temperature range of 500 – 700°C. The kinetic study of catalytic decomposition of biomass tars is represented using first order reaction. The results show that value of constant of chemical reaction is in range 0.2514 – 0.9642 cm<sup>3</sup>gr<sup>-1</sup>.min<sup>-1</sup> with value of the frequency factor (A) and the activation energy (E) are 48.98 min<sup>-1</sup> and 5724.94 cal.mol<sup>-1</sup>, respectively.

## INTRODUCTION

Energy is a primary need for all nations, so the demand of energy will continuously increase with increasing the growth of population. In next years, due to the shortage of fossil fuels, renewable energy sources will play an important role of energy shares. One of them, biomass is the promising resource of renewable energy because of abundant, inexhaustible and friendly environmental materials [1]. Many technologies have been developed to convert biomass sources to energy, such as combustion, pyrolysis, gasification, liquefaction etc. [2,3]. Among them, pyrolysis has several advantages compared to other processes, including: a simple reactor configuration, the faster reaction time, more liquid products (less energy for product separation) and adaptive to various types of biomass [4,5]. Tar formation is one of the major problems in pyrolysis process, because it causes operational problems such as the contamination in the inner wall of a reactor, blockages in pipes, formation of tar aerosols, carcinogenic and polymerization into more complex structures [6-8].

Tar is a complex mixture of acids, aldehydes, ketones, alcohols, phenols and aromatic hydrocarbons whose composition depends on the condition of pyrolysis [9]. Several methods have been proposed for removing tar such as absorption-adsorption, thermal and catalytic decomposition. Chemical conversion by catalytic decomposition is more attractive because of cheaper and easier operation. The study of tar decomposition using several alkali metal catalysts such as olivine, dolomite, limestone, metal oxides, Ni, Pt, Rh and Pd was performed [10-14]. The main problem of catalyst is carbon deposition in the pores, which decrease catalyst activity [15]. The iron-oxide-based catalyst such as Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> could be used effectively for tar decomposition to produce syngas [16,17]. It has also been reported that the natural iron ore was useful for tar decomposition to produce clean syngas with tar content less than 0.01% [5].

The propose of this research is to study kinetics of catalytic decomposition of biomass tars. We used Indonesian iron ore as catalyst. It is well-known that Indonesia has abundant resources of iron ore but a main part of Indonesian iron ore is low grade iron ore (total Fe <60% mass). Direct utilization of low grade iron ore in steel-making industries is thermally disadvantageous because it requires high energy consumption compared to commercial high

grade ore due to large content of combined water [18,19]. By using low grade iron ore as catalyst of tar decomposition, tar carbon infiltrated and deposited within the pores of the iron ore, which could act as reducing agents. The distance between carbon and iron atoms was very closed so this process resulted in high reduction rate, low reduction temperature and low energy consumption.

### Kinetic Model

The following assumptions are considered to develop this model: (1) The fixed bed reactor is in steady state operation. (2) The reaction takes place on isothermal condition. (3) The reactions are all catalytic, the thermal conversion and diffusion to the axial direction is not taken into account.

Based on the above assumptions, the mass balance equation for tar decomposition in fixed bed reactor with the incremental length of reactor can be written:

$$V_z \frac{dC_T}{dz} = -(-r_T \cdot \rho_b) \quad (1)$$

The reaction of tar decomposition was modelled as a single reaction:



Assuming a first-order reaction, the formal reaction rate becomes:

$$r_T = -k \cdot C_T \quad (3)$$

Thus, coupling Equations (1) and (3) become:

$$V_z \frac{dC_T}{dz} = -(k \cdot C_T \cdot \rho_b) \quad (4)$$

Where  $C_T$  is the concentration of gravimetric tar, expressed as mass per volume,  $V_z$  is superficial velocity ( $\text{cm}^3/(\text{cm}^2 \cdot \text{s})$ ) and  $\rho_b$  is bulk density of the catalyst ( $\text{g}/\text{cm}^3$ ),  $k$  is the reaction rate constant expressed by the Arrhenius's equations, as in:

$$k = A \cdot \exp \left[ -\frac{E}{RT} \right] \quad (5)$$

where  $A$  is frequency factor ( $\text{min}^{-1}$ ) and  $E$  = activation energy ( $\text{cal}/\text{mol}$ )

Since Equation (4) is differential equation, Runge-Kuttamethod is chosen to solve them numerically. The parameter of  $k$  is evaluated by trial and error until ones giving the minimum values of the Sum of Squares of Error (SSE) for run data. The SSE was defined as:

$$SSE = \sum ((C_i)_{simulation} - (C_i)_{data})^2 \quad (6)$$

The parameter of  $A$  and  $E$  will be found by modify Equation (5) become straight-line equation as follow:

$$\ln(k) = A - E \cdot \left( \frac{1}{RT} \right) \quad (7)$$

## MATERIALS AND METHODS

### Materials

Tar used in this study was derived of pyrolysis from wood waste with heating value 28.77 MJ/kg and density 1.009  $\text{gr}/\text{cm}^3$ . While iron ore was obtained from PT. SILO (Sebuku Iiril Laterit) in Sebuku Island, Kotabaru, South Kalimantan, Indonesia. The compositions of iron ore were 51.41 % of total Fe, 7.214 % of  $\text{Al}_2\text{O}_3$ , 3.042 % of  $\text{SiO}_2$  and 0.423 % of NiO.

The ore was crushed and sieved to obtain a sample with similar particle sizes ranging from 2 to 2.8 mm. To order to obtain a high surface area and porous material, the iron ore was dehydrated at 500 °C at a heating rate of 3 °C/min and holding time 2 h in air atmosphere.

## Apparatus

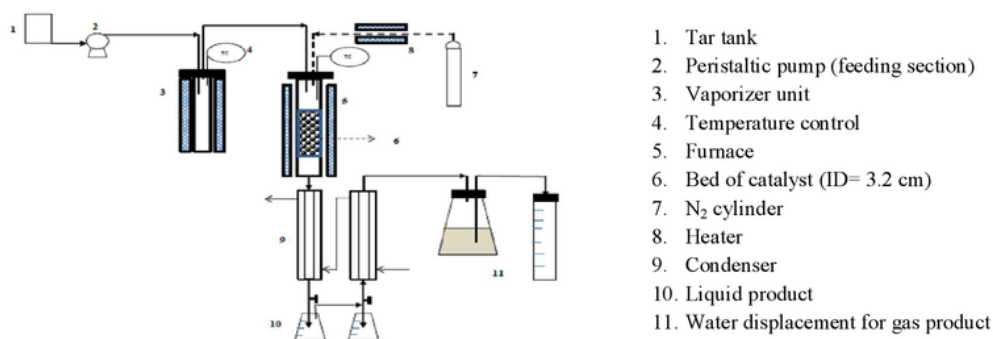


FIGURE 1. Experiment apparatus for tar decomposition

Fig. 1 shows the experimental equipment for tar catalytic decomposition. The experiments were performed in a fixed bed reactor filled with iron ore catalyst at atmospheric pressure and range temperature of 500 - 650 °C. The apparatus was equipped with a vaporizer to ensure the oil enters the reactor in the vapor phase and a condenser set to change condensable vapor to liquid.

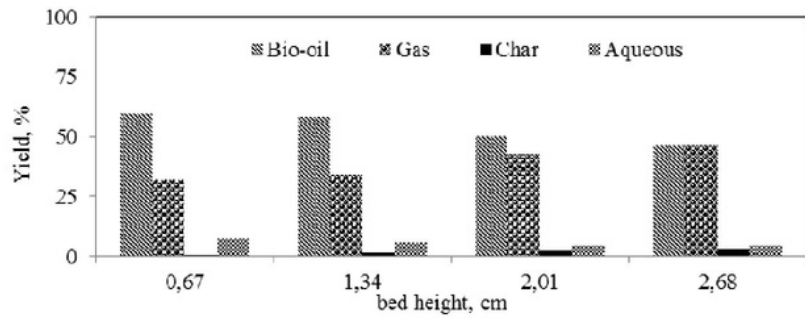
## Experiment Procedure

The experiment runs were started by passing nitrogen through the reactor and preheater to remove oxygen. The furnace and vaporizer were heated by electric heater and the temperature was controlled by digital temperature controller. After the temperature inside the reactor and vaporizer reached steady condition at specified temperature, the tar was flowed into the vaporizer to vaporize the tar. Then, the tar vapor will pass through the catalyst bed. The catalytic reaction occurred inside the reactor, producing char, tar vapor and gases. Subsequently, the vapor and gases left the reactor and entering the cooling system to condense tar vapor. There are two phases which obtained from the condenser, the aqueous and the organic liquid phase. The gas volume is measured by the displacement volume of water. The compositions of the liquid and gas product were analyzed using Gas Chromatography and GC-MS.

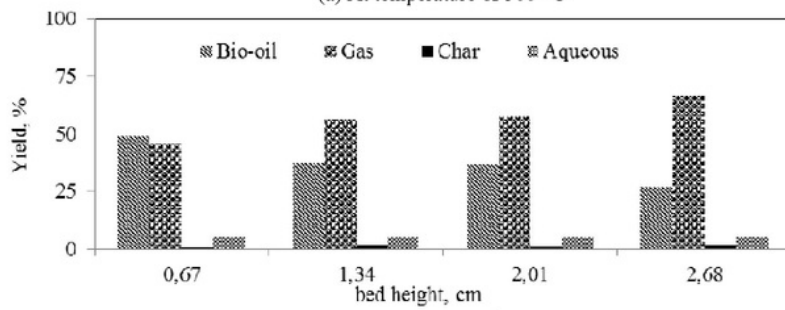
## RESULT AND DISCUSSION

### Effect of temperature and length of reactor

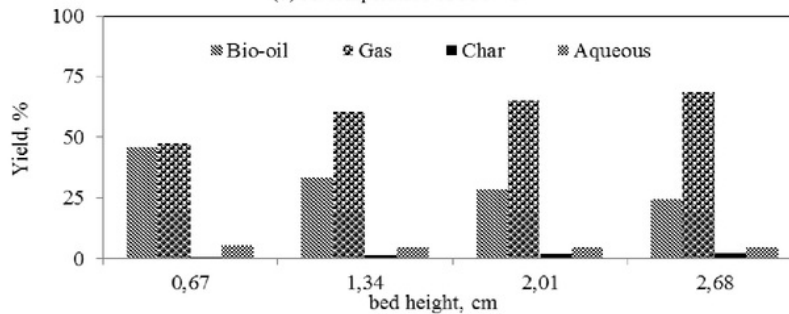
The experimental results were obtained from tar decomposition in a fixed bed reactor. In this study, the tar decomposition produce liquid products, gas, aqueous and coke formation. Fig. 2 presents the yields of bio-oil, gas, aqueous, and coke at different temperature and length of reactor over Indonesian iron ore.



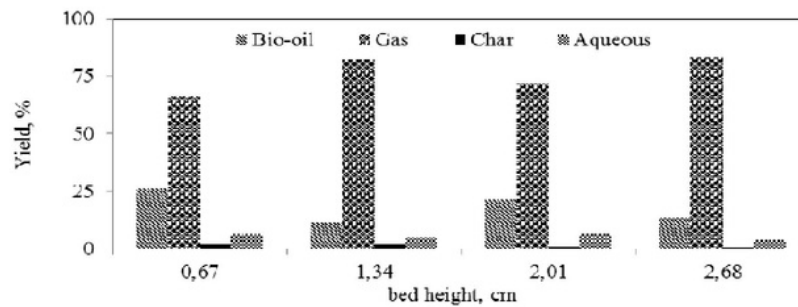
(a) At temperature of 500 °C



(b) At temperature of 550 °C



(c) At temperature of 600 °C



(d) At temperature of 650 °C

FIGURE 2. Yield of products from tar decomposition over Indonesian iron ore catalyst at different temperature

From Fig. 2, we may see that while temperature and bed height increased, yield of bio-oil decreased, yield of gas increased and yield of aqueous remained relatively stable. Yield of char increased slightly with increasing bed height at temperature of 500 – 600 °C and decreased at temperature of 650 °C. It indicated that the tar compounds, heavy and light hydrocarbon, were decomposed and cracked become gases, light hydrocarbon (bio-oil) and carbon, resulting in decreased tar content in bio-oil and increased the total gas product.

### Kinetics of tar decomposition

Obtained value of k at different temperatures was listed in Table 1. From this table, it was seen that the rate reaction constant increased with increasing temperature. This result is a gree with the Arrhenius's law.

TABLE 1. The reaction rate constant at tar decomposition

Temperature (°C)	k(cm <sup>3</sup> /gr. min)	SSE
500	0.2514	0,0047
550	0.4387	0,0064
600	0.6492	0,0054
650	0.9642	0,0036

To calculate the values of A and the E then graphed the relationship between ln (k) and  $\frac{1}{T}$ , as shown in Fig. 3. From this figure, it was obtained the linear equation as:

$$\ln(k) = 2881,2\frac{1}{T} + 48,98 \quad (9)$$

From Equation (9), the point of intersection with the y-axis is ln (A) and tangent direction is  $\frac{E}{R}$ . It was then obtained the values of A and E were 48.98 min<sup>-1</sup> and 5724.94 cal/mol, respectively.

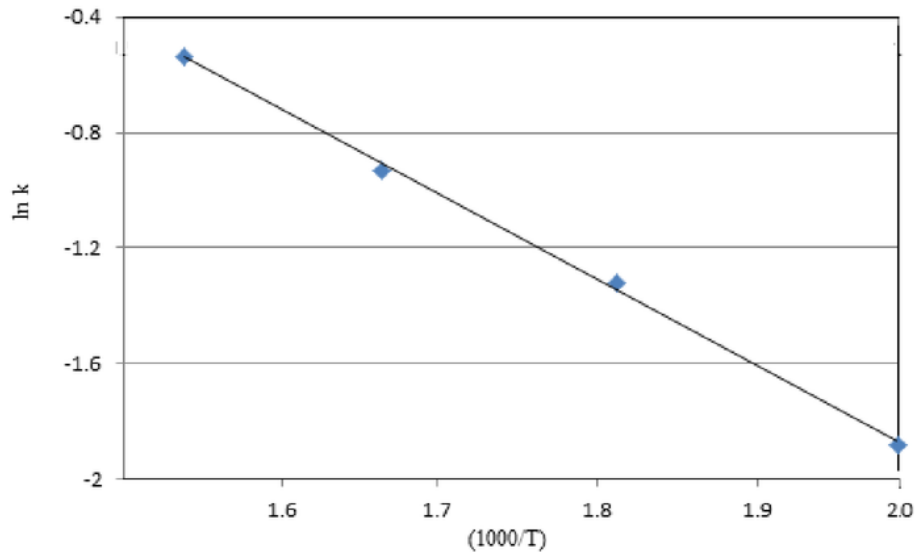


FIGURE 3. Temperature dependency of the reaction rate constant of tar decomposition according to Arrhenius' law

Fig.4 presents the concentration of biomass tar for experimental and simulated data at different length and temperature. It was seen that the kinetics model proposed is able to well describe the phenomena of biomass tar decomposition.

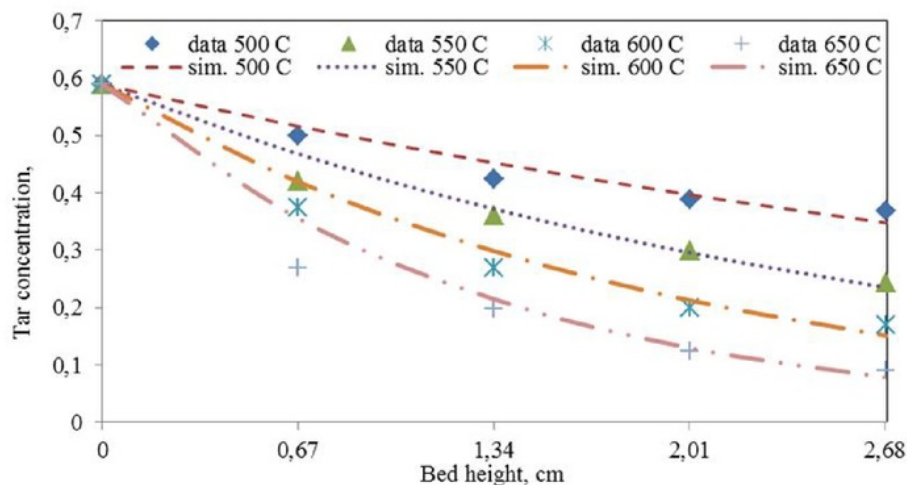


FIGURE 4. Experimental and simulated data for tar decomposition

## CONCLUSION

From this study, it can be concluded that:

1. Catalytic decomposition of biomass tar can be simplified to be a first order reaction.
2. The value of reaction rate constant follows Arrhenius equation with constant of chemical reaction is in range  $0.2514 - 0.9642 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$  and value of the frequency factor (A) and the activation energy (E) are  $48.98 \text{ min}^{-1}$  and  $5724.94 \text{ cal} \cdot \text{mol}^{-1}$ , respectively.

## REFERENCE

1. Daniyanto, Sutijan, Deendarlianto and A. Budiman. *AIP Conf. Proc.* **1699**, 030017 (2015).
2. N. Laksmono, M. Paraschiv, K. Loubar, and M. Tazerout, *Fuel Processing Technol.* **106**, 776–783 (2013).
3. H. Dewajani, Rochmadi, S. Purwono, and A. Budiman, *JESTEC* **10** (7), 61-69 (2015).
4. A.M. Widiyannita, R.B. Cahyono, A. Budiman, Sutijan and T. Akiyama, *AIP Conf. Proc.* **1755**, 050004 (2016).
5. S. Kudo, K. Norinaga, and J. Hayashi, *J Novel Carbon Res Sci* **6**, 1-8 (2012).
6. M.A. Uddin, H. Tsuda, S. Wu, and E. Sasaoka, *Fuel* **87**, 451- 459 (2008).
7. Y. Shen and K. Yoshikawa, *Renew. Sust. Rev.* **21**, 371 – 392 (2013).
8. T. Furusawa and A. Tsutsumi, *Appl Catal A: Gen* **278**, 207-12 (2005).
9. T.A. Milne, N. Abatzoglou, and R.J. Evans, *Biomass Gasifiers Tars: Their Nature, Formation and Conversion*, U.S. Department of Energy, 1998.
10. D.A. Constantinou, J.I.G. Fierro, and A.M. Efstathiou, *Appl. Catal. B-Environ.* **90**, 347-359 (2009).
11. D.A. Constantinou, J.I.G. Fierro, and A.M. Efstathiou, *Appl. Catal. B-Environ.* **95**, 255-269 (2010).
12. H. Noichi, A. Uddin, and E. Sasaoka. E., *Fuel Process. Technol.* **91**, 1609-1616 (2010).
13. M. Virginie, C. Courson, D. Niznansky, N. Chaoui, and A. Kiennemann, *Appl. Catal. B: Environ.* **101**, 90-100 (2010).
14. B.F. Zhao, X.D. Zhang, L. Chen, R.B. Qu, G.F. Meng, X.L. Yi, and L. Sun. *Biomass Bioenerg.* **34**, 140-144 (2010).
15. R.B. Cahyono, A.N. Rozhan, N. Yasuda, T. Nomura, S. Hosokai, Y. Kashiwaya, and T. Akiyama, *Fuel Process Technol.* **113**, 84 – 89 (2013).
16. M. Barati, S. Esfahani, and T.A. Utigard, *Energy* **36**, 5440 – 5449 (2011).
17. A. Uddin, H. Tsuba, S. Wu, and E. Sasaoka, *Fuel* **87**, 451 – 459 (2008).



18. R.B. Cahyono, A.N. Rozhan, N. Yasuda, T. Nomura, S. Hosokai, Y. Kashiwaya and T. Akiyama, [Fuel Process Technol.](#) **113**, 84 – 89 (2013).
19. D.R. Wicakso, Rochmadi, Sutijan, and A. Budiman, [AIP Conf. Proc.](#) **1737**, 060009 (2016).

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