

## Catalytic Pyrolysis of Rice husk via Semi-batch Reactor using L9 Taguchi Orthogonal Array

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**Abstract.** The market demand of bio-fuel is 11,8 billion liters based on recent reported data. Hence, with the high demand of bio-fuel, the bio-fuel production utilizing rice husk can be one of the solutions. Beside, bio-oil can be produced by pyrolysis process utilizing rice husk as the feedstock. In this research, the optimization condition in producing bio-oil from rice husk by catalytic pyrolysis process was studied. The effect of catalyst type (H-β, H-Y, HZSM-5), catalyst loading (1wt%, 5wt%, 12wt%), temperature (400-500°C) and flow rate (60-100ml/min) were investigated through repetitive experiments using L9 Taguchi Orthogonal Array. The highest liquid yield of 38wt% was obtained at the optimum conditions with temperature of 500°C with nitrogen flow rate of 60ml/min and 12wt% of H-ZSM-5.

### Introduction

Nowadays, the world is facing depletion of energy source. Currently, human life and activities are mainly depending on fossil fuel based products such as gasoline, diesel, liquefied petroleum gas and natural gas. Oil consumption has increased dramatically from 1.84 (million barrels per day) in 1984 to 5.27 (million barrels per day) in 2008. Consequently, the global oil production is decreasing very fast and will be lower than 40% by 2075[1]. In addition, climate change and high fuel prices are critical problems faced by the world. Therefore, biofuel emerges to be an alternative energy substitute for fossil fuels. Biofuel is a green fuel with negligible amount of nitrogen and sulfur. Therefore, it will release a low emission of SO<sub>2</sub>, H<sub>2</sub>S, NO, NO<sub>2</sub> and the CO<sub>2</sub> release from bio-fuel can be taken up by the plants via photosynthesis [2].

Currently, the first generation of bio-fuels is produced mainly from plant which is suitable for food. This is not good because some parts of the Earth's population are suffering from hunger or malnutrition. Therefore, scientists proposed the "Second Generation" technologies for the production of fuels. This generation produces bio-fuel from non-food/inedible "cellulosic" biomass feedstock. These include agricultural residues (e.g. rice husk, forest, straw, bagasse, corn stover), wastes (e.g. paper, cardboard, manures, sawmill residues) and specially grown energy crops (e.g. miscanthus, willow, switch grass). [3-5].

Rice husk is the outer covering of paddy and accounts for 20-25% of its weight. The estimated annual world rice production is about 571 million tons; with the rice husk is about 140 million tons. This amount is available for utilization. In Malaysia, it is estimated over 9 million tons of rice waste generated annually from rice milling industry [6]. Therefore, utilization of this source of waste via energy recovery has the potential to solve waste management problem and also generates useful energy.

Pyrolysis is a thermal degradation process, which decomposes organic material at high temperature with absent of oxygen [7]. The liquid and gas product from pyrolysis are hydrocarbon and can be used as fuel [8]. They also known as bio-oil has the potentials to be used as a promising future energy source. Beside that catalysts is used to study the decomposition reaction that reduces the oxygenate content via de-oxygenation reaction to improve the calorific value of the bio-oil with better hydrocarbon distribution. This improves the quality and stability of bio-oil [9-13]. For the catalytic pyrolysis the relative distribution of catalyst type, catalyst loading, reaction temperature and nitrogen flowrate which are the most influential were studied.

In this paper, the catalytic pyrolysis of rice husk is investigated. The optimum condition which produces the maximum liquid yield was found based on different types of catalyst, catalyst loading, reaction temperature and nitrogen flowrate using the Taguchi's L9 Orthogonal Array. The properties of the bio-oil obtained at the optimum reaction condition were characterized and compared by other researchers [14].

## Materials and Methodology

### Materials and Sample characterization

#### Rice husk

The particle size of the ricehusk was reduced with a Cutting Mill and was sieved to a particle size of 250  $\mu\text{m}$  - 500  $\mu\text{m}$ . The rice husk was dried in the oven at 105  $^{\circ}\text{C}$  for at least 24 hours before being used in the catalytic pyrolysis experiments. The rice husk properties is listed in Table 1.

The proximate analysis including moisture, combustible matter and ash was determined using Thermogravimetric analyzer EXSTAR TG/DTA 6300. In addition, the ultimate analysis obtained by using CHNS Analyzer, LECO (Model 932) based on the ASTM D5291 standard. Oxygen content was determined by difference of the value obtained from CHNS analyse and the heating value was measured using IKA C5000 Bomb Calorimeter. Moreover, Inductively Couple Plasma – Atomic Emission Spectroscopy (ICP-AES) analysis shows the elementary components are P, K, Ca, Mg, Cu, Fe, Mn, Zn, Na, Al, Ti and Si.

Table 1: Proximate analysis of rice husk

Characteristics	Value
<b>Proximate analysis</b>	
Moisture (wt%)	2.01
Combustible matter (wt%)	86.63
Ash (wt%)	11.36
<b>Ultimate analysis</b>	
C (%)	38.85
H (%)	4.89
N (%)	1.07
S (%)	0.15
O (%)	55.04
<b>Heating value (J/g)</b>	15244.33
<b>ICP-AES analysis (mg/kg)</b>	
Phosphorus (P)	439
Potassium (K)	3093
Calcium (Ca)	303
Magnesium (Mg)	323
Copper (Cu)	4
Iron (Fe)	173
Manganese (Mn)	46
Zinc (Zn)	26
Sodium (Na)	<1177
Aluminum (Al)	85
Titanium (Ti)	<1.0
Silicon (Si)	1747

### Zeolites

The zeolite catalysts used in this study are obtained from Zeolyst International. Their properties are summarized in Table 2.

Table 2: Properties of zeolite catalysts used

Type of catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Surface Area (m <sup>2</sup> g <sup>-1</sup> )
H-ZSM-5	30	400
H-Beta	25	680
H-Y	30	780

### Pyrolysis process

The experimental setup is as stated in [15]. The catalytic cracking experiments were performed in a semi-batch reactor which was heated externally by an electric vertical furnace. Temperature was valued referring to L9 Taguchi Orthogonal Array. A thermocouple was used to measure the temperature inside the reactor.

15g of biomass was filled in the borosilicate tube. The zeolite catalyst was weighed accordingly as indicated in Table 3 and mixed thoroughly with the bio-oil. The tube was tighten and purged for 5 minutes with nitrogen gas flow of 500 ml/min. A flow controller was used to control the nitrogen gas flow. After 5 minutes of degassing, the nitrogen flow was set at the desired flow rate and the furnace was heated at 20°C/min of the heating rate. Gas from the reaction is carried out by nitrogen and passed through a condenser with the temperature maintained at 0°C. The reactor was left to cool to room temperature after the completion of each run. The tube was weighed after the reaction to identify the weight of the bio-char produced after the reactions.

The procedures were repeated at different condition of variables setting based on Taguchi L9 Orthogonal Array as shown in Table 3.

Table 3: L9 Taguchi orthogonal Array

Run	Type of Catalyst	Catalyst Loading (wt %)	Temperature (°C)	Nitrogen Flow Rate (ml/min)
1	H-β	5	450	80
2	H-ZSM-5	5	400	100
3	H-β	12	500	100
4	H-Y	5	500	60
5	H-β	1	400	60
6	H-Y	1	450	100
7	H-Y	12	400	80
8	H-ZSM-5	1	500	80
9	H-ZSM-5	12	450	60

L9 Orthogonal Array has been developed using Design Expert 8.0.6.1 software. The total of experiments needed to achieve the outlined objectives is nine. These nine experiments which were based on Taguchi method helped in the systematic approach for data analysis and identification of parameters that affect the oil production. The relationship between the variables was established using the Design Expert software and analysis was conducted for each parameter. Additional experiment was made to verify the optimum parameters and reactions time required to achieve the optimum process condition.

The equations used to calculate the yield are:

$$W_{liquid} = W_{condenser-after} - W_{condenser-before} \quad (1)$$

$$W_{gas+liquid\ product} = W_{rice\ husk} - W_{residue} \quad (2)$$

$$Conversion = \frac{W_{gas+liquid\ product}}{W_{rice\ husk}} \times 100 \quad (3)$$

$$Selectivity_{liquid\ product} = \frac{W_{liquid}}{W_{gas+liquid\ product}} \times 100 \quad (4)$$

$$Yield_{liquid} = (Selectivity_{liquid\ product} \times Conversion) / 100 \quad (5)$$

$$Yield_{gas\ product} = Conversion - Yield_{liquid\ product} \quad (6)$$

Where W = weight (g)

## Result and Discussion

In Table 4, the weight of gas+liquid product, the conversion, selectivity liquid yield and gas yield were calculated base on equations (1), (2), (3), (4), (5) and (6). The conversion of pyrolysis process is high since the obtained value is above 60wt%. This result shows that the pyrolysis process was successfully conducted in the developed single step reactor. Besides, the liquid product yields were obtained from 31.08wt% to 38wt%. The highest liquid product yield of 38.00wt% obtained is at run number 9 by using 12wt% of H-ZSM-5, nitrogen flow rate of 60ml/min and temperature of 450°C. On the other hand, the highest gas product yield of of 31.28wt% is at run number 6 with the operating condition set at 100 ml/min of nitrogen flow rate, temperature of 450°C and 1wt% of catalyst H-Y. This result shows that each factor has different effect on the yield.

Table 4: Experimental results and (wt%) Signal to Noise Ratio (S/N)

Run	$W_{liquid\ product}$ (gram)			$W_{gas+liquid}$ product (gram)	Conversion (wt%)	Selectivity (wt%)	Yield <sub>liquid</sub> product (wt%)	Yield <sub>gas product</sub> (wt%)	S/N
	1 <sup>st</sup> round	2 <sup>nd</sup> round	Average						
1	5.09	5.21	5.15	9.390	62.63	54.82	34.33	28.30	27.70
2	5.05	5.24	5.15	9.19	61.29	55.98	34.31	26.98	27.69
3	5.31	5.3	5.30	9.75	64.98	54.46	35.39	29.59	27.97
4	5.52	5.51	5.51	9.63	64.17	57.30	36.77	27.40	28.30
5	5.48	5.08	5.28	9.05	60.33	58.34	35.20	25.13	27.90
6	4.91	4.41	4.66	9.35	62.36	49.84	31.08	31.28	26.80
7	5.40	5.27	5.34	9.19	61.28	58.07	35.59	25.69	28.01
8	5.41	5.39	5.40	9.44	62.93	57.20	36.00	26.93	28.12
9	5.75	5.65	5.70	9.50	63.30	60.03	38.00	25.30	28.58

Signal to Noise Ratio (S/N) is a variance index which can be used to identify the most optimum condition by selecting the highest S/N value. There are three quality characteristics considered, “the smaller the better”, “the nominal the best” or “the bigger the better”. For this experiment, the “the bigger is better” was defined as the determining factor was verifying to the yield of liquid product. The value of S/N was shown in Table 4. The greater the value, the smaller the product variance compared to the target value [16]

The equation to calculate the S/N is:

$$\frac{S}{N} = -10 \log_{10} \left( \frac{1}{n} \times \sum \frac{1}{y^2} \right) \quad (6)$$

where  $r$  is the number of tests in a trial,  $y_i$  is the experimental response at  $i^{\text{th}}$  repetition. In order to examine the significance of each individual factor on the liquid yield, the average S/N value for each factor  $f$  at level  $j$  is computed for each factor and level, as shown in equation (7):[17,18]

$$\frac{S}{N} = \frac{\text{Sum of S/N values for factor } i \text{ at level } j}{3} \quad (7)$$

The range of S/N ratio values ( $\Delta$ ) is calculated for each factor and a larger range signifies a higher influence on the liquid yield.

Table 5: S/N ratio values for each factor and level

Level	Type of catalyst (A)	Catalyst Loading (B)	Reaction Temperature (C)	Nitrogen Flowrate (D)
1	27.86	27.61	27.87	28.26
2	27.70	27.90	27.70	27.94
3	28.13	28.19	28.13	27.49
Range ( $\Delta$ )	0.43	0.58	0.43	0.77
Rank	4	2	3	1

Based on the S/N ratio, the rank or the efficiency of the factors was determined. In Table 5, the Delta value is the highest for nitrogen flowrate (factor D). Hence, it is found to have the highest effect on the yield of liquid product (bio-oil) because a change in the factor causes a larger impact on the liquid yield, resulting in a larger S/N ratio range ( $\Delta$ ). The second higher effect that influences the yield of liquid product is Catalyst type (factor A) with a Delta value of 0.58. Next is the Reaction Temperature (factor C) followed by the Type of catalyst (B) with Delta value of 0.432 and 0.426 respectively, showing less significance on the outcome of the experiments.

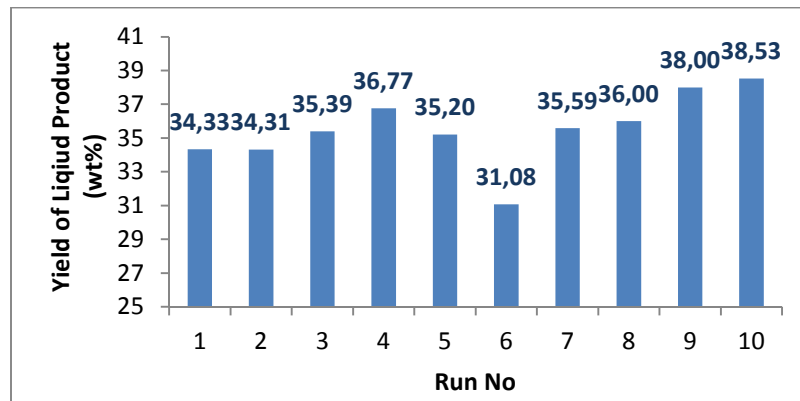


Figure 1: Yield of liquid product in condenser

Figure 1 shows the highest yield of liquid product can be observed for run number 9 with the operating conditions of nitrogen flow rate of 60ml/min, temperature of 450°C and 12wt% of H-ZSM-5. However, the optimum operating conditions are 60 ml/min of nitrogen flow rate, temperature of 500°C and 12wt% of H-ZSM-5 with the predicted yield of 39.58wt%. As a consequence, an experiment run 10 was conducted at the predicted optimum conditions to validate the liquid yield proposed by software. Based on run 10, the liquid yield is 38.53wt% which is close to the predicted liquid yield. The prediction for the optimum condition by the Taguchi software has been proven to produce the highest yield of OLP. In the other hand, this result was comparable with M.S. Abu Bakar et al.(2012) research which liquid yield is 38.29wt% using the couple reactors [19].

## Conclusion

The influences of factors such as type of catalyst, catalyst loading, reaction temperature and nitrogen gas flowrate on the liquid (bio-oil) yield was studied. The Taguchi L9 Orthogonal Array Method was used to determine and predict the optimum reaction condition. The optimum operating conditions are at 60 ml/min of nitrogen flow rate, temperature of 500°C and 12wt% of H-ZSM-5 with the yield of 38.53wt%.

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