

## PHYSICAL CHARACTERIZATION AND DESULFURIZATION OF BIO-BRIQUETTE USING CALCIUM-BASED ADSORBENT

Mahidin<sup>1\*</sup>, Asri Gani<sup>1</sup>, and Khairil<sup>2</sup>

1. Department of Chemical Engineering, Faculty of Engineering, University of Syiah Kuala, Banda Aceh 23111, Indonesia
2. Department of Mechanical Engineering, Faculty of Engineering, University of Syiah Kuala, Banda Aceh 23111, Indonesia

\*<sup>1</sup>E-mail: mahidin@unsyiah.ac.id

---

### Abstract

Combustion of coal and co-combustion of their co-fuel contribute to gas emissions. Among the gas emissions are SO<sub>x</sub>, NO<sub>x</sub>, CO and CO<sub>2</sub>. Introduction of calcium based adsorbent is addressed to absorb SO<sub>2</sub> that release to the atmosphere during the combustion process. Objective of the research is at first to observe the physical characteristics of bio-briquettes as a function of briquette compositions (coal to palm kernel shell ratios) and Ca/S ratios (Ca in adsorbent and S in briquette) using a natural adsorbent (shellfish waste). The second objective is to investigate desulfurization characteristics as a function of Ca/S ratios and desulfurization temperatures at coal to palm kernel shell ratio of 90:10 (wt %). Ratios of coal to palm kernel shell in this study are 90:10, 80:20, 70:30, 60:40 and 50:50; and Ca/S ratios are 1:1, 1.25:1, 1.5:1, 1.75:1 and 2:1. Binding agent used is the mixture of *Jatropha curcas* seeds and starch as much as 10% (wt). It was found that introducing the palm kernel shell and adsorbents in the coal briquette affect the water resistant and compressive strength. The highest water resistance and compressive strength were 5,165 second and 34 kg/cm<sup>2</sup>, respectively. The lowest SO<sub>2</sub> level found in this study was 1 ppm for all Ca/S ratios, except for 1:1.

*Keywords: bio-briquettes, calcium-based adsorbent, Ca/S ratio, coal/palm kernel shell ratio, desulfurization*

---

### 1. Introduction

Energy crisis faced by Indonesia may affect all sectors such as education, economics, social and politics. Therefore, to solve the problems, work should be focused on efforts to find the renewable alternative energy sources in order to fulfill energy demand. One candidate of the renewable alternative energy sources is palm kernel shell (PKS) which is abundant in Indonesia. Indonesia is estimated to produce about 146.7 million tons of biomass per year, equivalent to 470 GJ/year. The main sources of biomass derived from agricultural waste, wood waste, and waste from plantation activities and waste from processing unit of agriculture and plantation crops.

Currently, the utilization of biomass, especially in rural areas is limited to direct combustion, without any pre treatment, which may lead to various problems. Besides, the direct combustion of bulk biomass produces low thermal efficiency. Use of bulk biomass directly for cooking is usually having negative impact on air quality that can affect health. Therefore, it needs a clean and efficient method to convert bulk biomass waste to a source of energy effectively and efficiently

so that rural communities can safely use the energy for house hold or home industry purposes.

On the other hand, Indonesia has also total coal reserve as much as 38.9 billion tones (proven 6.98 billion tones). More than 65% of the reserve is not utilized yet and more than 83% is low-rank coal such as sub-bituminous and lignite. Since the low-rank coal has high sulphur content, therefore use that coal as a single fuel especially in home industry or household will raise a number of problems during the combustion, for example SO<sub>x</sub> emissions. These reflect use of coal unsafe and unattractive because cooking stoves are generally used without chimneys. In order to make coal become more attractive, the above mentioned problems should be solved first.

During the past two decades, there have been a number of studies to improve the quality of coal briquettes by various method such as carbonizing the coal before briquetting [1-2] or adding lime-based adsorbent (CaO) into coal briquettes [3-16]. An industrial briquette produced from mixture of hard coal, molasses pulp and hydration limestone gives an effective SO<sub>2</sub> reduction in a 46.5 MW traveling grate furnace [4]. Desulfurization

efficiency of bio-briquettes is strongly influenced by coal type and it varies in the range 25–67% [8]. It is reported that a SO<sub>2</sub> reduction of 40% from the flue gas is obtained in a 4 t/h traveling grate furnace when treated CaCO<sub>3</sub> is added into coal briquette [9]. Excellent results have shown by Osuwan et al., Naruse et al. and Wang et al. [5,7,10-11] that SO<sub>2</sub> emissions are reduced by 75-95% during the combustion of bio-briquettes as compared to low-rank coal.

Moreover, it is observed that briquette prepared under lower molding pressure with finer sorbents has a better desulfurization capability. Calcium hydroxide and scallop shell both have better desulfurization capabilities than limestone; because calcium hydroxide has lower calcination temperature and scallop shell has larger porosity after calcinations. Also, adding some alkali or transition metal compounds into limestone could increase desulfurization efficiency during coal briquette combustion [3,6-7].

Objective of the research is to observe physical characteristics of bio-briquettes as a function of bio-briquette compositions (coal/PKS ratios) and Ca/S ratios (Ca in adsorbent and S in bio-briquette) using natural adsorbents (shellfish waste). Additionally, it is also examined desulfurization characteristics as a function of Ca/S ratios and oxidation temperatures at the coal/PKS ratio of 90:10 (wt %).

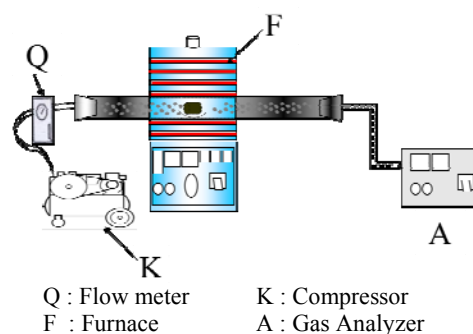
**2. Methods**

The study was conducted at the following conditions: briquette diameter is 20 mm, hold pressing time is 5 minutes, the content of starch (tapioca-based) and jatropha seeds as a binding agent in briquette is 10% of the briquette weight [17], briquetting pressure was 6 ton/cm<sup>2</sup>. Ratios of coal/PKS are 90:10, 80:20, 70:30, 60:40 and 50:50 (in weight) and ratios of Ca/S are 1:1, 1.25:1, 1.5:1, 1.75:1 and 2:1 (in mole). Particle sizes are -60/+pan mesh. The following Table 1 presents the

**Table 1. Proximate and Ultimate Analysis Data for Low-Rank Coal and PKS**

|                  | Unit (adb) <sup>*)</sup> | Coal  | PKS   |
|------------------|--------------------------|-------|-------|
| <b>Proximate</b> |                          |       |       |
| Moisture         | %                        | 5.83  | 4.30  |
| Ash              | %                        | 5.40  | 2.63  |
| Volatile Matter  | %                        | 46.00 | 73.65 |
| Fixed Carbon     | %                        | 42.77 | 19.42 |
| <b>Ultimate</b>  |                          |       |       |
| Carbon           | %                        | 60.65 | 29.32 |
| Hydrogen         | %                        | 5.75  | 5.88  |
| Nitrogen         | %                        | 0.48  | 0.30  |
| Total Sulphur    | %                        | 0.38  | 0.13  |
| Oxygen           | %                        | 27.34 | 61.74 |
| Calorific Value  | kcal/kg                  | 5,904 | 4865  |

<sup>\*)</sup>adb = air dried base



**Figure 1. Schematic Diagram of Experimental Apparatus**

proximate and ultimate analysis of low-rank coal and PKS. Meanwhile, shellfish waste used in this research has Ca content of 27.8% (wt).

Before briquetted, coal, PKS and jatropha seeds were crushed, sieved and mixed to produce homogenous mixture (here starch was also added to the mixture). After mixed, the sample then was put into the mold to be pressed using a machine press with a pressure of 6 ton/cm<sup>2</sup>. Compressive strength test is performed by using Computer Type Universal Testing Machine. In the water resistance examination, the 500 ml of water at room temperature used to immerse the briquettes, and measure the time required for the briquettes destroying and dispersion in the water [18].

Finally, desulfurization test was attempted by using horizontal pipe furnace attached with electrical heater element. Bio-briquette sample was put inside the pipe. Desulfurization temperatures were 350-500 °C. Flue gas was analyzed directly at interval time of 1, 3, 6, 9 and 12 minutes using Gas Analyzer Model E 4400-S. Schematic diagram of experimental apparatus is shown in Figure 1.

**3. Results and Discussion**

Results and discussions are present in two subsections: (i) physical characteristics such as compressive strength and water resistance tests, and (ii) desulfurization characteristics observation.

**Compressive strength and water resistance.** One of characterizations of the briquettes is compressive strength test to examine the compressive resistance of briquettes [17-19]. In the application, compressive force may attached during transportation or storage. Figure 2 shows the effect of coal/PKS ratio on the strength of briquettes, although the effect is not significant and without any tendency/pattern. The highest and the lowest compressive strengths have shown by the bio-briquette with Ca/S ratio of 2:1 at coal/PKS ratios of 60:40 and 50:50, i.e. 0.34 and 0.08 kg/mm<sup>2</sup> (34 and 8 kg/cm<sup>2</sup>), respectively.

In Indonesian standard, the parameter of compressive strength is not included, whereas it is included for example in UK standard (i.e. 12.7 g/cm<sup>2</sup>) and Japan standard (i.e. 60-65 g/cm<sup>2</sup>) [17]. It is seen that all briquettes produced in this research met both UK and Japan standards, even the lowest one (i.e. 8 kg/cm<sup>2</sup> or 8000 g/cm<sup>2</sup>). These results reflect that the mixture of tapioca-based starch and jatropha seeds is good enough to use as a binding agent in briquettes production. In the previous study we have already examined the use of single binder for both tapioca-based starch and jatropha seeds in producing biomass briquettes without adsorbent. It was obtained that both binders could produce the high compressive strengths briquettes. All the observed compressive strengths were higher than 27 kg/cm<sup>2</sup> [20].

Further, from Figure 2 it is seen that interesting phenomena are presented by bio-briquettes at coal/PKS 50:50 in which the compressive strength are decreased for all Ca/S ratios. This may cause by the weak bonding between coal particles and PKS or between PKS particles themselves since the PKS content is high enough in this case. If it is confirmed to previous study [20], thus, first assumption that the bonding between coal particles and PKS is weak becomes more reasonable.

Water resistance parameter is measured by immersing the briquettes into water at room temperature. The water resistance defined as the time required for briquettes being destroyed and dispersed in water, then briquette which is destroyed faster means having a weaker structure. The influence of coal/PKS ratio is proved; the water resistance slows down when PKS content increased. It is expected that, PKS structure is more hydrophilic compare to coal structure and/or coal

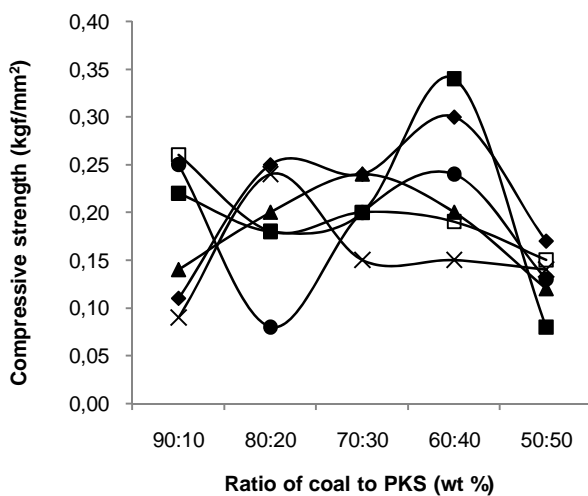


Figure 2. Compressive Strength of Bio-briquettes for Various Coal/PKS at Ca/S Ratios of 1:1 (♦), 1.25: 1 (▲), 1.5:1 (x), 1.75:1 (●), 2:1 (■) and no Adsorbent (□)

structure more hydrophobic than PKS structure. This is just an assumption which needs adequate investigation on the structure of coal and PKS in order to prove the above mentioned statement.

In this study, it is found that the strong bio-briquettes that can be used in small industries/household are the bio-briquettes produced using 90% coal at Ca/S ratio 1:1 with the required time for being destroyed and dispersed in water is 5,165 second (Figure 3). Briquettes with 90% of coal are more feasible to use in terms of the water resistance. In addition, the effect of adsorbent is also clear when comparing bio-briquettes produced using adsorbent to bio-briquettes produced without adsorbent. It should be noted that the data present here agreed well to the data reported by Yaman et al. [18] for biomass-lignite coal briquettes at various compositions.

Effect of coal/PKS and Ca/S ratios are not really demonstrated for compressive strength of bio-briquettes, and fortunately it gives clear effect for water resistance, which is the strong bio-briquettes are obtained at coal/PKS ratio of 90:10 for all Ca/S ratios. Therefore, desulfurization study was then only conducted for these entire bio-briquettes.

**Desulfurization characteristics.** Combustion of each bio-briquette contributed to different SO<sub>2</sub> concentrations in the flue gas. Sulfur was oxidized during combustion of coal to produce SO<sub>2</sub> gas.

Calcium based adsorbent was calcinated and then captured SO<sub>2</sub> gas with the folowing reactions.

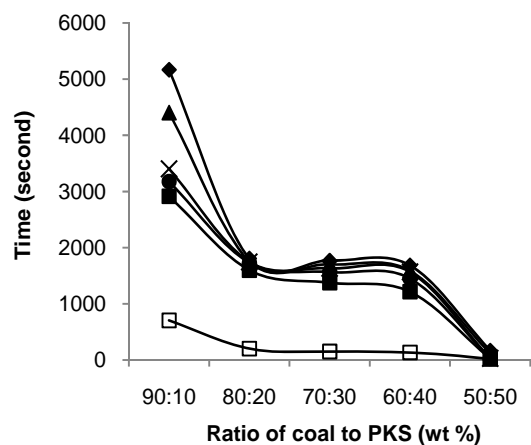
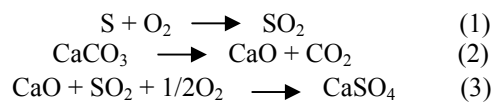


Figure 3. Water Resistance of Bio-briquettes for Various Coal/PKS at Ca/S Ratios of 1:1 (♦), 1.25: 1 (▲), 1.5:1 (x), 1.75:1 (●), 2:1 (■) and no Adsorbent (□)

The SO<sub>2</sub> level may depend on the Ca/S ratios and desulfurization temperatures. Profiles of SO<sub>2</sub> for various Ca/S ratios and desulfurization temperatures are shown in the following Figures 4-7.

It is seen that, as expected, SO<sub>2</sub> concentrations decreased with an increase of Ca/S ratio. All the data clearly exhibit the influence of Ca on the reduction of SO<sub>2</sub> and leveled off when Ca/S was 2 at 350 °C, when Ca/S was ≥1.5 at temperatures 400-450 °C and when Ca/S was ≥1.25 at temperature 500 °C. It reveals that the self-desulfurization can be realized by mixing the desulfurizer/adsorbent into bio-briquette. Moreover,

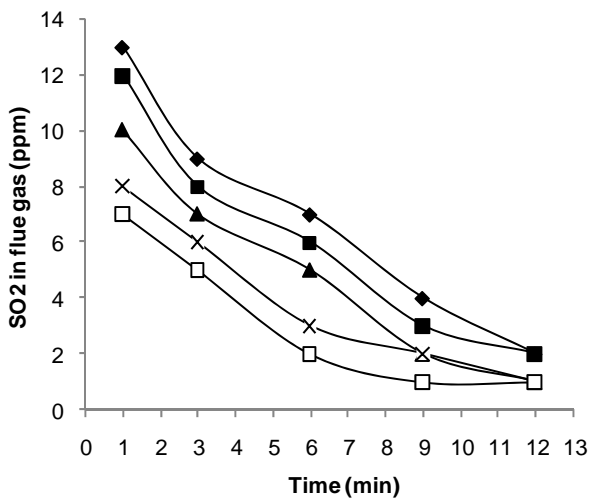


Figure 4. Profile of SO<sub>2</sub> in Flue Gas During the Combustion of Bio-briquettes at 350 °C for Ca/S Ratios of 1:1 (♦), 1.25: 1 (■), 1.5:1 (▲), 1.75:1 (×), 2:1 (□)

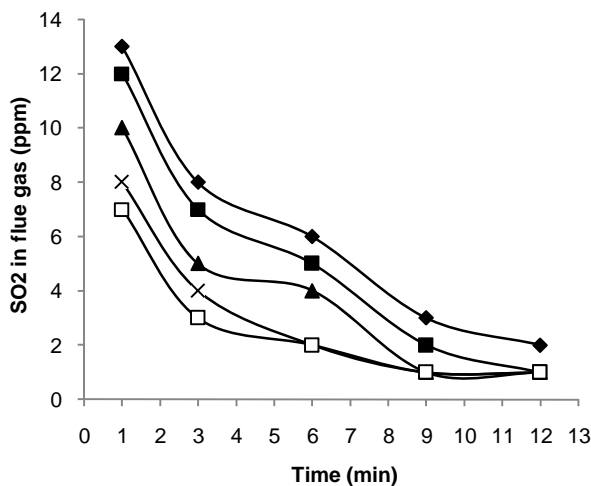


Figure 5. Profile of SO<sub>2</sub> in flue gas during the Combustion of Bio-briquettes at 400 °C for Ca/S Ratios of 1:1 (♦), 1.25: 1 (■), 1.5:1 (▲), 1.75:1 (×), 2:1 (□)

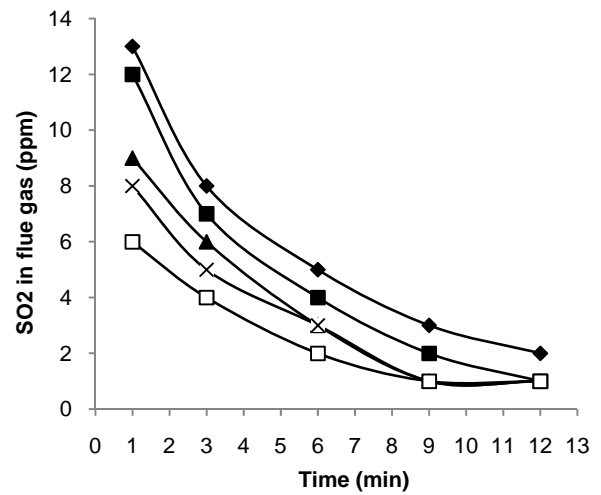


Figure 6. Profile of SO<sub>2</sub> in Flue Gas During the Combustion of Bio-briquettes at 450 °C for Ca/S Ratios of 1:1 (♦), 1.25: 1 (■), 1.5:1 (▲), 1.75:1 (×), 2:1 (□)

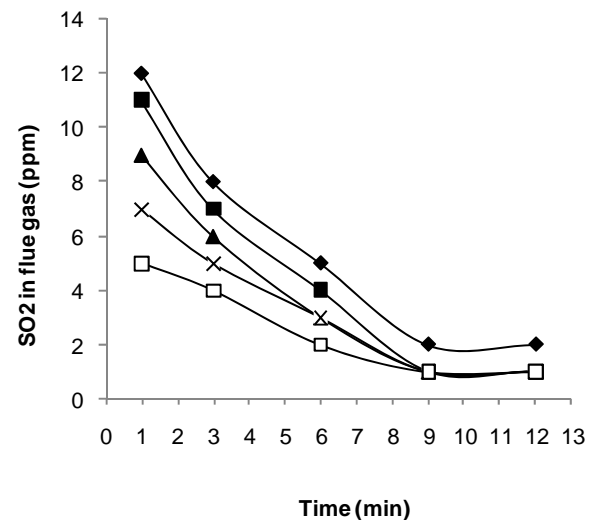


Figure 7. Profile of SO<sub>2</sub> in Flue Gas During the Combustion of Bio-briquettes at 500 °C for Ca/S Ratios of 1:1 (♦), 1.25: 1 (■), 1.5:1 (▲), 1.75:1 (×), 2:1 (□)

the facts also reflected the effect of desulfurization temperature on SO<sub>2</sub> profiles. The results in this study might improve the previous observation [10-13,15-16], even Ca content in shellfish adsorbent is much lower than those in scallop shell and limestone adsorbents.

Another advantage of this adsorbent is that the desulfurization/calcination temperatures were lower enough (<500 °C) compare to others adsorbent such as limestone (>800 °C) and scallop shell (>625 °C) and similar to calcium hydroxide (400 °C) [7,12]. Therefore, both limestone and scallop shell seem to have difficulty

in capturing SO<sub>2</sub> under the temperature lower than 600 °C. The difference in desulfurization ability between shellfish and limestone or scallop shell may be a result from differences in pore structure after calcinations. Before use, shellfish waste was subjected to calcinations process at 800 °C. However, pore structure for shellfish is not observed yet.

#### 4. Conclusion

Based on the results and discussions mentioned above, it is concluded that the bio-briquettes produced at coal/PKS ratio of 90:10 provide better water resistance performance. In the desulfurization effectiveness point of view, bio-briquettes with Ca/S ratio of 2:1 give a significant lower level of SO<sub>2</sub> emission in flue gas during bio-briquettes combustion. Therefore, it is recommended to use the bio-briquettes with the coal/PKS ratio of 90:10 and Ca/S ratio of 2:1 in small industries or household.

#### Acknowledgements

This study was funded by Directorate General of Higher Education, Ministry of National Education through The Hibah Penelitian Strategis Nasional with the contract number 516/SP2H/PP/DP2M/VII/2010. Thank is addressed to the student who performed the laboratory work: Ernawati, Rini Wahyuni, M. Reza Hani, Muhammad Syukur and Kamarullah.

#### References

- [1] K. Bunyakiat, S. Osuwan, A. Potjanart, Proceedings of the Third World Congress of Chem. Eng., Tokyo, Japan, 1995, p. 541.
- [2] K. Bunyakiat, S. Osuwan, A. Wuttimongkolchai, Proceedings of the Forth Asian Pacific Confederation of Chem. Eng. Congress, Singapore, 1995, p.95.
- [3] J.Z. Liu, Y.Q. Cao, X.H. Zhang, Power Eng. 12/2 (1992) 35 (in Chinese).
- [4] K. Kleisa, J. Lehmann, F. Verfuss, G. Simon, Glueckauf-Forschungshefte 55/4-5 (1994) 117.
- [5] S. Osuwan, K. Bunyakiat, D. Theerapabpisit, J. Sci. Soc. Thailand 15 (1995) 17.
- [6] C.M. Lu, S.Q. Cheng, Y.L. Shao, H.X. Zhao, H.Y. Gong, Proceeding of Int. Conference Energy Environ, New York, U.S.A., 1996, p.667.
- [7] I. Naruse, H. Kim, G. Lu, J. Yuan, K. Ohtake, Proceedings of the Twenty-Seventh Symposium (International) on Combustion, Pittsburgh, U.S.A., 1998, p.2973.
- [8] G. Lu, H. Kim, J. Yuan, I. Naruse, K. Ohtake, M. Kamide, Energy Fuels 12/4 (1998) 689.
- [9] Y.Z. Ren, J.F. Dong, Y.Q. Cao, J.Q. Qian, J. Eng. Thermophys. 20/1 (1999) 125 (in Chinese).
- [10] J. Wang, S. Gao, W. Wang, K. Sakamoto, J. Aerosol Res. 14/2 (1999) 162.
- [11] Q. Wang, G. Lu, K. Sakamoto, T. Maruyama, H. Kim, I. Naruse, S. Hatakeyama, T. Mizoguchi, R. Luo, M. Kamide, J. Aerosol Res. 15/4 (2000) 364 (in Japanese).
- [12] G. Lu, Q. Wang, K. Sakamoto, H. Kim, I. Naruse, J. Yuan, T. Maruyama, M. Kamide, M. Sadakata, Energy Fuels 14/6 (2000) 1133.
- [13] K. Sakamoto, S. Gao, W. Wang, J. Wang, I. Watanabe, Q. Wang, J. Japan Soc. Atmospheric Env. 35/2 (2000) 124.
- [14] P. Siritheerasas, K. Bunyakiat, S. Osuwan, Thammasat Int. J. Sci. Technol. 5/2 (2000) 34.
- [15] X. Dong, K. Sakamoto, W. Wang, S. Gao, Y. Isobe, J. Env. Sci. 16/5 (2004) 705.
- [16] K. Yamada, A. Sorimachi, Q. Wang, J. Yi, S. Cheng, Y. Zhou, K. Sakamoto, Atmospheric Env. 42 (2008) 7924.
- [17] A.M. Fauzi, S.E. Agustina, J.I. Nugraheni, Industri: J. Ilmiah Sains dan Tek. 9/1 (2010) 75.
- [18] S. Yaman, M. Şahan, H. Haykiri-Açma, K. Şeşen, S. Küçükbayrak, Fuel Processing Technol. 72 (2001) 1.
- [19] N. Kaliyan, R.V. Morey, Biomass and Bioenergy 33 (2009) 337.
- [20] Mahidin, A. Gani, Subhan, F. Iznita, I. Agustina, Industri: J. Ilmiah Sains dan Tek. 10/1 (2011) 35.