Biomass as a fuel source has been widely investigated over the last few years. Biomass includes wood waste and agricultural residues such as rice husks and waste sugar sediment, and among others. Gasification is an easy method to produce combustible gases from biomass, producing hydrogen, carbon monoxide and methane which could be used in industrial applications requiring heating. In the case of the mushroom grower, boiling water is necessary in the production activities, and heat is also required for other production processes. Using biomass waste to generate heat and other biofuel sources is considered one alternative effort to make the business become more efficient and competitive. Molino et al. (2018) knew that the gasification of biomass can produce synthetic natural gas (SNG) and hydrogen.

Waste mushroom substrate (WMS) was abundant in surrounding environment. The production of WMS may reach 1,000 kg/day from a medium scale mushroom production unit. The substrate cannot be used for growing a crop of mushrooms and cannot use it again (Fig. 1). Transporting the material was considered costly and in long period, the substrate may become hazardous to the environment (Basu, 2010a; Wang, Wang, Cao, & Wang, 2010; Yoon, Son, Kim, & Lee, 2012).

In this study, a quantity of WMS, and the pellets, referred to here as WMSP, were used as the biofuel to produce CH$_4$ in an updraft gasifier. The WMS was made from composted rubber wood chips which had been used for mushroom bed log culture, and pelleting the WMS (WMSP) to create a biomass with a greater bulk density than the normal WMS. The gasification was determined in the high temperature range of 400-800 °C by dry fuel feeding at the rate of 25 kg/ha. The results showed that the optimum operation was achieved with WMSP with K$_2$CO$_3$ as the catalyst, at ER = 0.11. The combination of WMSP and K$_2$CO$_3$ produced more CH$_4$ at 62.2 and 15.27% than single WMS and WMSP, respectively. WMSP with CaO as the catalyst produced 29.65 % less CH$_4$ than WMSP. Based on gasification equation, CO produced from WMSP was calculated 24.116 % wt, 31.52% wt from WMSP with K$_2$CO$_3$ and 19.21% wt from WMS. The amount of gas produced from the available waste material as the biomass was sufficient to meet all heating requirements of the mushroom production.
Sirikul Saengsuwan and Somchai Kritpolwiwattana: Gas Production Waste Mushroom Substrate

CO₂, at 700 °C. The catalysts, K₂CO₃ and Ca(OH)₂, as catalysts to the feeder material and varying rates of air flow were tested and the volume of methane in the gas produced was compared. The aim of the study is to evaluate pelletized WMS (WMSP) using catalysts of K₂CO₃ and Ca(OH)₂ to produce ecofriendly biofuel energy.

MATERIALS AND METHODS

Sampling
The gasification fuel used in this research was waste mushroom substrate (WMS) produced from rubber wood chips supplied by a timber company in southern Thailand, which had been used for growing mushrooms in a local mushroom growing business.

Pre-Treatment: Drying and Pelletizing
The WMS was pre-treated by drying with the extruder. A quantity of the WMS was pelletizing to form WSMP. WMS is relatively uniform in respect of shape of particles and chemical composition. This enabled simple contact between oxygen and the material and also allowed efficient combustion.

The Ultimate Analysis of the waste mushroom substrate pellets showed that it was composed of C (Carbon) (38.55% wt), H(Hydrogen) (6.46% wt), O(Oxygen) (54.17% wt), and S (Sulfur) (0.017% wt). Based on the proximate analysis, WSP material had moisture content of 29.91% from dry weight, 64.9% volatiles and 0.67% ash, Fixed Carbon (4.52%) with higher heat value of 15,395.97 kJ/kg, and bulk density (238.8 kg/m³). The Proximate Analysis used for the particle size was in accordance with ASTMD-1102 and ASTM E871-82, which was less than 475 microns. The Ultimate Analysis was done by x-ray and CHNS analysis from Suranaree University of Technology Thailand. The properties of the WMS are presented in Table 1.

Fig. 1. The rubber wood chips for growing mushrooms (a,b), packaged rubber wood chips, and wasted mushroom substrate (c,d)
Gasification Process

The gasification system used was an updraft gasifier filter designed by Assoc. Prof. Somchai Klittapolwiwat of Naresuan University Thailand (Fig. 2). The gasifier was constructed as an inner cylinder within the outer cylinder. The inner cylinder was wrapped in asbestos to insulate against heat loss. The feeder material, introduced through the top of the gasifier at a rate of 25 kg/h. Air flow was provided by a blower located near the bottom of the gasifier. Testing was carried out at three air flow rates 60, 45, and 30 Nm$^3$/h under atmospheric pressure. The temperature achieved in the gasification process was recorded 800-1000 °C.

In the combustion chamber, the combustible material was reduced to ash by pyrolysis. The gases in the combustion chamber were at varied temperatures indicating the different levels within the chamber which are identified as 1 to 5 in the diagram at Fig. 2. At level 5, the gas temperature was approximately 500 °C. In these condition, some tar containing many hydrocarbon molecules was generated. The cooler gas (< 500 °C) was extracted by gas producer located at the top of chamber and accumulated through the pipe labeled as 7 in Fig. 2. The composition of these gases was tested and measured by the ECOM J2KN. Before ECOM J2KN process, the gas was cleaned by filtering to avoid damage to the equipment.

The measurement of CH$_4$, CO$_2$ and O$_2$ was conducted and recorded every 3 minutes at ER = 0.11 (at point 6 Fig. 2) and the CO content was calculated using the following gasification equation (1-5) (Basu 2010b):

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 - 394 \times 10^3 \text{Jmol}^2 \\
C + 0.5O_2 & \rightarrow CO - 111 \times 10^3 \text{Jmol}^1 \\
C + CO_2 & \rightarrow 2CO - 172 \times 10^3 \text{Jmol}^1 \\
C + H_2O & \rightarrow CO - 131 \times 10^3 \text{Jmol}^1 \\
C + H_2 & \rightarrow CH_4 - 74.8 \times 10^3 \text{Jmol}^1
\end{align*}
\]

The equation for measuring CH$_4$ were estimated using the formula:

\[9.21 \times C + 3.07 \times H_2 \rightarrow 12.28 \times CH_4\]

The equations for using the two catalysts are:

\[
\begin{align*}
40.212 K_2CO_3 + 5.84 C & \rightarrow 15.592 K + 39.347 CO \\
9 CaO + 11 CO_2 & \rightarrow 20 CaCO_3
\end{align*}
\]

Table 1. The properties of waste mushroom substrate

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ultimate analysis (wt % dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash 67 % wt</td>
<td>C = 22.457</td>
</tr>
<tr>
<td>Volatile matter 64.9 % wt</td>
<td>H = 2.123</td>
</tr>
<tr>
<td>Fixed Carbon 6.78 % wt</td>
<td>N = 0.613</td>
</tr>
<tr>
<td>Moisture 29.91 % wt</td>
<td>And the others; P$_2$O$_5$ = 5.035, Ar =1.323</td>
</tr>
<tr>
<td>HHV 15,395.97 kJ/kg</td>
<td>K$_2$O= 8.795, CaO = 81.613, MnO$_2$ = 1.083</td>
</tr>
<tr>
<td>Bulk density 238.8 kg/m$^3$</td>
<td>Fe$_2$O$_3$ = 1.320, CuO = 0.452, ZnO = 0.109</td>
</tr>
<tr>
<td>Bulk density in pellets 79.6 kg/m$^3$</td>
<td>Percent by weight</td>
</tr>
</tbody>
</table>

Remarks: wt = weight

Fig. 2. Figure of gasifier

![Diagram of gasifier](image-url)
AI210 temperature gauge with K-type thermocouple was used to measure the temperature at the side of gasifier at six points (1-5 and 6 on the diagram in Fig. 2). The operational conditions are summarized in Table 2.

The Composition of the Produced Gases

At ER = 0.11, the volume of CH$_4$ produced from WMSP was 38.35% greater than those from WMS. This result is in accordance with the results reported by Chen, Annamalai, Ansley, & Mirik (2012) who found the amount of produced gas was depended on the size of the biomass particles. Theerarattananoon et al. (2011) also reported that the amount of produced gas was depended on the density of the bulk biomass. Kaewluan & Pipatmanomai (2011) used 100 mm in width x 5 mm in thickness rubber wood chips and successfully showed that gasification from rubber wood chip biomass feed can produce adequate amounts of electricity and savings in the cost of the fuel.

The amount of CH$_4$ produced with three air flow rates (60, 45, 30 Nm$^3$/h) were compared. WMSP with air flow rate of 60 Nm$^3$/h produced 22.15% greater volume of CH$_4$ than that with 45 Nm$^3$/h, yet 44.81% less than with an airflow rate of 30 Nm$^3$/h. The ER values were recorded 0.11 at air flow rate of 60 Nm$^3$/h, 0.15 at air flow rate of 45 Nm$^3$/h and 0.22 at airflow of 30 Nm$^3$/h. The percentage of CH$_4$ were observed 8.97, 4.95 and 8.20 at the air flow rate of 60, 45 and 30 Nm$^3$/hr (Fig. 3).

Table 2. The operational conditions of the experiment

<table>
<thead>
<tr>
<th>Gasification Conditions</th>
<th>Finding/Measuring/Calculating</th>
<th>Raw material biomass feeding rate</th>
<th>Air Flow Rate</th>
<th>ER</th>
<th>CO</th>
<th>CO$_2$</th>
<th>CH$_4$%</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMSP 50 kg/2h 60 Nm$^3$/hr 0.11</td>
<td>Calculate</td>
<td>ECOMJ2KN</td>
<td>Al210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WMSP 50 kg/2h 45 Nm$^3$/hr 0.15</td>
<td>ECOMJ2KN</td>
<td>Al210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WMSP 50 kg/2h 30 Nm$^3$/hr 0.22</td>
<td>ECOMJ2KN</td>
<td>Al210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WMSP 50 kg/2h 60 Nm$^3$/hr 0.11</td>
<td>ECOMJ2KN</td>
<td>Al210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WMSP+K$_2$CO$_3$ 50 kg/2h 60 Nm$^3$/hr 0.11</td>
<td>ECOMJ2KN</td>
<td>Al210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WMSP+CaO 50 kg/2hr 60 Nm$^3$/hr 0.11</td>
<td>ECOMJ2KN</td>
<td>Al210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Methane CH$_4$ production at three air flow rates: 60, 45, 30 Nm$^3$/h
RESULTS AND DISCUSSION

The average content of CH₄, CO₂, and O₂ and calculated CO using gasification equation 1-5 was presented in Table 3.

The indication of cracking reaction was the increasing level of hydrogen (Sheeba, Babu, & Jaisankar, 2009). A large amount of yield gas hydrogen maximally produced at the temperature of 1028.6 °C, but the H₂ yield decreased when ER increased. Gordillo, Annamalai & Carlin (2009) reported the use of gasification on cattle and diary biomasses to produce CO and H₂ for power generation. They found that gasification in cattle biomass manure (cattle biomass/CB and coal), under higher ER, yielded higher levels of CO and CH₄ and lower levels of H₂ and CO₂. While at higher air steam ratio (ASTRs), a mixture of poor H₂, CO₂, CH₄ lower HHV with rich in CO was produced. It was also found that a Fixed Bed gasifier using dairy biomass (DB). The wasted of food for animals in this experiment is called cattle dairy biomass or DB. Coal which is sub bituminous in Wyoming and lignite from Texas in America. Gordillo & Annamalai (2010) suggested that the wasted food for animals can produce gases enough for the power generation and the process could mitigate the wasted substrates about 56 metric tons per year. The paper presented the results of fixed bed gasification with steaming air as oxidizers and used the wasted food for animals. At the peak temperature, the energy conversion efficiency of carbon monoxide was lower, but higher for hydrogen and carbon dioxide. The equivalent ratio between the steamings of the fuel ratio and the higher heating value, and heat energy influenced the gases yield.

Previous study by Min et al. (2013) found that for ER not less than 0.25, the CH₄ increased with using catalyst and the CO₂ decreased. Similar results were reported by Karatas, Olgun, Engin, & Akgun (2013) with a difference ER between 0.15 and 0.45.

The value of CO was determined by comparing the values of CH₄, CO₂, and O₂. When there was no catalyst with the pellets, the CO was observed at 24.16% wt. The volume of CO produced from all conditions was presented in Table 3.

The Catalyst

CH₄ produced from an air flow of 60 Nm³/h given two catalysts K₂CO₃ and CaO with WMSP were compared. Catalyst K₂CO₃ increased CH₄ by 15.27, yet CaO tended to diminish CH₄ by 29.65% (Fig. 4). These findings was in accordance with Wang, Wang, Cao, & Wang (2010) in that calcium oxide as an earth metal had weaker catalytic activity in gasification than potassium carbonate as a alkali metal catalyst. Potassium carbonate which mixed in WMSP produced higher methane than WMSP without catalyst.

Ahmed & Gupta (2010) reported that CO and H₂ could be produced from the following 4 conditions: (1) temperatures of 800°C and 900°C, together with (2) the reaction time of carbon char and (3) with either of the two catalysts K₂CO₃ and Na₂CO₃, and (4) the flow rate of gas. They used leftover food and paper as the biomass in the gasification process, which resulted in the production of CO and H₂ with the value of 0.077 and 0.175 g/min, respectively, and there is higher gas production rate than in the process of pyrolysis oil Krzysztof twice and the catalyst in the process gases Pacific. Weerachanchai, Horio, & Tangsatthikulclai (2009) used two materials (larch and cellulose capsule) and 3 bed materials (silica, calcium limestone and calcine waste concrete). Their study showed that larch wood with bed material silica sand, calcium limestone and calcined waste concrete gave a large amount of gas hydrogen and carbon dioxide but little carbon monoxide when they used silica sand. The optimum process to produce gas with larch was at temperature 650-750 °C.

Table 3. Comparison of gases content measured by ECOM J2KN and calculated using CO in the gasification equations

<table>
<thead>
<tr>
<th>Conditions</th>
<th>CO₂</th>
<th>CO</th>
<th>CH₄</th>
<th>O₂</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMSP with air flow rate 30 Nm³/hr</td>
<td>6.60</td>
<td>18.443</td>
<td>8.20</td>
<td>8.78</td>
<td>0.23</td>
</tr>
<tr>
<td>WMSP with air flow rate 45 Nm³/hr</td>
<td>5.97</td>
<td>23.55</td>
<td>4.95</td>
<td>10.93</td>
<td>0.23</td>
</tr>
<tr>
<td>WMSP with air flow rate 60 Nm³/hr</td>
<td>5.46</td>
<td>24.16</td>
<td>8.97</td>
<td>11.50</td>
<td>0.23</td>
</tr>
<tr>
<td>WMSP with air flow rate 60 Nm³/hr+K₂CO₃</td>
<td>4.48</td>
<td>31.52</td>
<td>10.34</td>
<td>17.80</td>
<td>0.23</td>
</tr>
<tr>
<td>WMSP with air flow rate 60 Nm³/hr+CaO</td>
<td>5.46</td>
<td>22.78</td>
<td>6.31</td>
<td>11.50</td>
<td>0.23</td>
</tr>
<tr>
<td>WMSP with air flow rate 60 Nm³/hr</td>
<td>6.65</td>
<td>19.2134</td>
<td>5.53</td>
<td>7.70</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Three structures in plants (cellulose, hemicellulose and lignin) with two catalysts (Ni-Zn-Al and Ni-Ca-Al) in the proportion 1:1 were used in this gasification process. In the second pyrolysis of gasification with lignin and Ni-Zn-Al generated maximum residue fraction and produced higher concentration of gases than cellulose (Wu, Wang, Huang, & Williams, 2013). Related to previous description, Min et al. (2014) stated that char structure is important as a catalyst.
Temperatures in the Actual Gasifier were Measured at Fixed Locations

Fig. 5 and Fig. 6 showed the second point \( (T_2) \) is the best point to observe pyrolysis, with the temperature of 400-800 °C (Basu, 2010b). The first point \( (T_1) \) zone was the combustion zone which is very high temperature. The temperature at the \( T_2 \) zone and the \( T_3 \) zone are in the same range of 400-800 °C. The \( T_2 \) occurred in the range of 24-72 cm levels of cylinder, which is the pyrolysis reaction zone. Pyrolysis is the reaction that breaks down the large hydrocarbon molecules into smaller molecules. Temperature for pyrolysis is occurred between 425-600 °C. The primary pyrolysis took place at the temperature of 200-600 °C and occurred when the biomass decomposes into the primary char (Basu, 2010a). Dufour et al. (2008) stated that \( \text{CH}_4 \) increased up to 70% at 1000 °C and the tar decreased but gases increased at temperatures between 800-1000 °C (Commandré, Lahmidi, Salvador, & Dupassieux, 2011). Smaller char reacted to oxygen more easily in combustion and gasification. The type of gas produced from pyrolysis of wood was depended on the temperature within the range of 650-950°C. The higher pyrolysis temperature led to higher production of hydrogen. Ahmed & Gupta (2009) found that the gasification at high temperature produced higher amounts of synthetic gas (syngas).

The catalyst also affected the temperature in the reaction of pyrolysis and gasification at 800-900°C. Pattanotai, Watanabe, & Okazaki (2013) reported that tar as a catalyst was cracked at a temperature between 400-500°C. Pyrolysis of wood under steam at 750-850 °C produced high amount of \( \text{H}_2 \) and \( \text{CH}_4 \) (Kumar, Eskridge, Jones, & Hanna, 2009). Skoulou, Swiderski, Yang, & Zabaniotou (2009) also found that steaming as the gasifying agent of olive kernels at temperatures between 750-1050°C produced gases at 124.07 g/Nm³. Several reports regarding the temperature ranges of pyrolysis also included the carbonization as the secondary reaction in the pyrolysis at 800 °C (Hosoya, Kawamoto & Saka, 2007), increasing the moisture of the biomass led to decreasing the energy (Karamarkovic & Karamarkovic, 2010), increasing the temperature to between 600-900 °C in the gasification process, and using Ni and Al₂O₃ can increased \( \text{H}_2 \) from 3.2 to 13.1% (Elbaba & Williams, 2012).

Fig. 6. Comparison of the temperature during gasification reaction
Saravanakumar, Haridasan, Reed, & Bai (2007) used long sticks in the gasification process in an updraft gasifier with a volume of 0.714 m³ and 1.34 m in height, with the temperature of 750 °C. Biagini, Cioni, & Tognotti (2005) also found that this process produced the highest volume of cold gases. Matos, Nahas, Rojas, & Rosales (2011) studied the characteristics of carbon in Algarroba sawdust at a temperature of 800 °C with CO₂ and N₂ flow, which produced sufficient synthetic gases for potential novel applications. Couhert, Commandre, & Salvador (2009) found that by using soft or hard wood at higher temperatures increased the volume of gas. Gordillo & Annamalai (2010) reported that increasing the temperature in the gasification process produced higher CO₂ and H₂ volumes by an endothermic reaction. Karatas, Ölgun, Engin, & Akgun (2013) used waste tires in the fluidized gasifier at the pressure 1 atm and found that the ER varied in the range 0.15-0.45 (also affected by particle sizes) and lower CO₂ but higher CH₄. Hosoya, Kawamoto & Saka (2007) found that tar from wood polysaccharides underwent secondary reactions including carbonization after condensation with temperatures lower than boiling point in the gasification at 800 °C. Sheeba, Babu, & Jaisankar (2009) found that the increment of gas yield was in line with the increase of temperature. Vaezi, Passandideh-Fard, Moghiman, & Charmchi (2012) concluded that HHV and temperature mainly were effected by biomass oxygen content. Oxygen is necessary for oxidation reaction and Aljbour & Kawamoto (2013) showed higher H₂ was obtained by the increase of temperature and ER from 0 to 0.3. The amount of methane and the other little molecule of hydro carbon in the gasification reaction were depended on the temperature. Zhao et al. (2009) studied the performance of an entrained gasifier with rice husk as the biomass in the gasification at temperatures among 700 to 1000 °C with the equivalent ratio varies 0.22 from 0.34. They found that hydrocarbon substances cracked in the reaction of gasification at the temperature above 1000 °C. At the higher temperature the reaction between oxygen and char had a more prevailing role in the oxidation zone and the optimum value of ER was 0.25 was reached at the temperature above 800 °C. Min, Yimsiri, Asadullah, Zhang, & Li (2011) studied the second pyrolysis in the reforming in the reaction of biomass tar at temperatures of between 500-900 °C with Mallee wood as a biomass. They found the char that produced in the reaction with iron/nickel as catalyst induced to reform tar and use the catalysts to enhance their activity in reforming tar. Min et al. (2013) studied the different result of the second tar reaction using leaves, bark and wood from Mallee tree. The chemical compositions and tar yields were different among these substances as the temperature increased. They found that the ilmenite was a good activity for the reforming tars from the different parts of Mallee. They also studied the changes of tars during the activities of reforming. The structure of tars before and after reforming was characterized with Roman Spectroscopy (the instrument for investigation the structure of tar). The results showed that the catalysts changed easily after steam reforming with the size ranged at 800-1800 cm⁻¹. These showed the comparison of the larger and smaller aromatic ring system increase after reforming at temperature of 800 °C or higher which were important to deposit the char during reforming with catalysts.

CONCLUSION

The highest CH₄ produced was at ER = 0.11 with 450 g of K₂CO₃ given at 50 kg of MWSP. The volume of CH₄ was detected at 8.97% wt using WMSP only and increased by 18.62% after K₂CO₃ catalyst was added. The temperature in the pyrolysis reaction was between 400-800 °C. The process also produced 1 kg of tar and 0.96 kg of ash after burning the 50 kg of biomass. The pyrolysis reaction occurred at the temperatures range of 400-800 °C. Production of methane decreased by 42% with high smoke and tar when 450 g of CaO catalysts was supplemented in MWSP. MWSP produced 62.20% more methane than MWS.

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REFERENCES


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