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Gasification of Pelletized Corn Residues with Oxygen Enriched Air and Steam

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ABSTRACT This study worked generation of producer gas using oxygen-enriched air and steam mixture as gasifying medium. Corn residues consisting of cobs and stover were used as biomass feedstock. Both corn residues were pelletized and gasified separately with normal air, oxygen enriched air and steam mixture in a fixed bed reactor. Effects of oxygen concentration in enriched air (21\textendash 50\%), equivalence ratio (0.15\textendash 0.35), and steam to biomass ratio (0.0\textendash 0.8) on the yield of product gas, the combustible gas composition such as H\(_2\), CO, and CH\(_4\), the lower heating value (LHV), and the gasification efficiency were investigated. It was found that the decrease in nitrogen dilution in oxygen enriched air increased proportion of combustible gas components, improved the LHV of producer gas, but gasification efficiency was not affected. The increase in equivalence ratio favoured high product gas yield but decreased combustible gas components and LHV. It was also observed that introduction of steam enhanced H\(_2\) production but excessive steam degraded fuel gas quality and decreased gasification efficiency. The highest gasification efficiency of each oxygen concentration was at equivalence ratio of 0.3 and steam to biomass ratio of 0.58 for cob, and 0.22 and 0.68 for stover, respectively. © 2019. CBIORE-IJRED. All rights reserved

Keywords: Agricultural residues; Biomass energy; Producer gas, Thermochemical conversion, Renewable energy

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1. Introduction

Most common method of gasification is using air as reacting agent. This method is straightforward and very simple, requiring less capital and operating cost (Tippayawong et al., 2011; 2013). However, presence of inert nitrogen in air dilutes the gas and hence lowers the heating value per unit volume of gas. Oxygen agent involves expensive cost. Steam agent consumes large amount of energy for heating enough steam temperature and requires steam recovery system. Many researchers studied the ways to improve product gas quality. Wongsiriamnuay et al (2012; 2013) improve product gas by using catalyst in the process. The presence of catalyst was found to increase the amount of H\(_2\) and CO. However, catalyst recovery was required. Lv et al (2004) studied the characteristics of biomass air steam gasification in a fluidized bed. Compared with biomass air gasification, the introduction of steam greatly improved heating value (from 6.7 to 9.1 MJ/m\(^3\)), gas yield and carbon conversion efficiency. Campoy et al (2009) studied the effect of oxygen in the gasification agent by enriched air-steam biomass gasification in a fluidized bed gasifier. The oxygen content in the enriched air was varied from 21 to 40\%. The experimental result showed that the enrichment of air made it possible to increase the gasification efficiency from 54 to 68\% and the LHV of the gas from 5 to 9.3 MJ/m\(^3\), while reaching maximum carbon conversion of 97\%.

From previous studies, it was found that addition of steam can improve air gasification, the use of enriched air reduces the nitrogen dilution effect, improve product gas quality and gasification efficiency. Using enriched air steam mixtures as gasification agent has been found relatively rare. Moreover, many researchers investigated medium calorific value gas production from biomass gasification in a fluidized bed which is suitable for medium to large scale. Only a few studies explore medium calorific value gas production in small and medium scale fixed bed gasifier. Therefore, the focus of this work is small to medium-scale plant from biomass gasification in fixed bed gasifier by using oxygen enriched air-steam as gasifying
agent. These 21-50% O₂ content in air are chosen because they are the oxygen concentrations that can be produced using commercial air separators based on membrane technologies (Wang et al., 2005). Producing oxygen this way keeps the investment and operational costs relatively low, compared to processes that need high oxygen content above 50%, usually based on pressure swing adsorption or distillation units.

2 Materials and Methods

2.1 Sample preparation

Corn cob and stover were collected from agricultural areas in Nan, Thailand. The cob and stover were ground with hammer mill to reduce the size and screened particle to less than 3 mm. They were characterized results shown in Table 1, separately formed to pellet with cylindrical die and hydraulic piston with control pressure 200 MPa and temperature 80°C with 8 mm diameter to get EN 14961-2 standard (Wongsiriamnuay and Tippayawong, 2015). The pellet materials were subsequently dried at 103°C for 3 days to remove humidity and stored in a desiccator to control humidity.

2.2 Experimental setup and procedure

A laboratory scale fix bed gasifier was used in this study. It was modified in the previous setup (Wongsiriamnuay et al., 2013). Schematic diagram and picture of setup is shown in Figure 1. Its components consist of fixed bed reactor, sampling grate, temperature control, steam generator and air providing, gas cleaning unit, gas metering, gas sampling bag and gas offline analyzer. The reactor was made from stainless steel pipe. The height of the reactor was 105 cm and inside diameter of 55 mm. It was divided in two sections, the upper was cooling section, surrounded by cooling water. Temperature in this zone was not over 50°C. The lower was a heating section, surrounded and controlled by a 5 kW electrical heater with insulated covering. The reactor was installed with K-type thermocouples to control reactor temperature, monitor temperature of sampling biomass, gas in and gas out during reaction. The outlet of the reactor connects to the cleaning unit which consisted of 8 tubes of isopropanol and placed in -20°C ice bath for removing tar and other condensable in obtaining gas. The gas keeps absorbing humidity by silica gel and then passing to a volumetric gas meter for gas yield measuring. The meter was calibrated with bubble flow meter and rotameter before using. The gas was collected in multi-layer foil gas bag. At each experimental run, the reactor temperature was isothermally controlled at 800°C. About 15 g of samples was loaded in the sampling basket, placed in cooling section, hermetically seal and vacuum the reactor to remove out the air. The temperature in this zone was not over 40°C. After the temperature reached the desiring point and steady, the basket was moved down into the middle of the heating section. Gasifying agent such as air, oxygen-enriched air and steam were fed at the same time under various operating conditions of oxygen content (OC of 21, 30, 40, and 50% O₂), equivalence ratio (ER of 0.15, 0.2, 0.25, 0.3, and 0.35) and steam to biomass ratio (SB of 0, 0.2, 0.4, 0.6, and 0.8). The biomass was gasified together with collecting the gas for 15 min. After that, stop feeding

Fig. 1 Schematic of gasification setup.
the agents, move the basket up into cooling section together with nitrogen feeding to stop the reaction. After the process, the dried gas was measured by dry gas meter, the left solid was weighed, and the amount of liquid in the glass condenser was measured by taking the difference in mass before and after the test. The gas product was immediately analyzed to find the composition. This research focuses on gas production. The compositions of char and liquid productions were not analyzed in their composition.

### 2.3 Data analysis

Mass balance for the gasification process was checked. The mass of gas was calculated from

$$p_{gas}V_{gas} = m_{gas}RT$$

(1)

The gas chromatography model GC-8A, Shimadzu was used to analyze gas composition of H₂, O₂, N₂, CH₄, CO and CO₂ with Shin-carbon column and high purifying helium was carrier gas.

Gas lower heating value (LHV) which showed the quantity of heat released by combustion, a specific amount of fuel under normal condition, and gasification efficiency (η₉) which were the ratios of the heat content of the fuel gas generated by the gasification of the biomass and of the heat content of that biomass when it was totally burnt, were calculated by Eqs. 2 and 3, respectively.

$$LHV = 10.78\%H₂ + 12.63\%CO + 35.88\%CH₄$$

(2)

$$\eta_9 = \frac{V_{gas} \times LHV_{gas}}{m_{biomass} \times LHV_{biomass}} \times 100\%$$

(3)

### Table 1

Properties of corn cob and stover on dry basis (% w/w)

<table>
<thead>
<tr>
<th></th>
<th>Corn cob</th>
<th>Corn stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter</td>
<td>80.3</td>
<td>77.1</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>17.5</td>
<td>16.9</td>
</tr>
<tr>
<td>Ash</td>
<td>2.2</td>
<td>5.7</td>
</tr>
<tr>
<td>C</td>
<td>47.5</td>
<td>49.5</td>
</tr>
<tr>
<td>H</td>
<td>6.7</td>
<td>6.1</td>
</tr>
<tr>
<td>O</td>
<td>45.1</td>
<td>43.7</td>
</tr>
<tr>
<td>N</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

### Table 2

Regressions for each response

<table>
<thead>
<tr>
<th>Response (Y)</th>
<th>Regression equations, Y = f (OC, ER, SB)</th>
</tr>
</thead>
</table>

### Table 3

Ranges of experimental data

<table>
<thead>
<tr>
<th></th>
<th>For Air (21% O₂)</th>
<th>Corn cob</th>
<th>Corn stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (%)</td>
<td>5.47 ± 0.19</td>
<td>3.71 ± 0.45</td>
<td></td>
</tr>
<tr>
<td>CO (%)</td>
<td>6.56 ± 0.16</td>
<td>5.46 ± 0.17</td>
<td></td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>2.16 ± 0.67</td>
<td>2.38 ± 0.64</td>
<td></td>
</tr>
<tr>
<td>LHV (MJ/m³)</td>
<td>3.09 ± 0.75</td>
<td>2.83 ± 0.47</td>
<td></td>
</tr>
<tr>
<td>Gas efficiency (%)</td>
<td>34.94 ± 0.74</td>
<td>33.11 ± 0.49</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>For 30%, O₂</th>
<th>Corn cob</th>
<th>Corn stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (%)</td>
<td>7.31 ± 0.20</td>
<td>7.23 ± 0.22</td>
<td></td>
</tr>
<tr>
<td>CO (%)</td>
<td>8.33 ± 0.17</td>
<td>6.34 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>3.29 ± 0.35</td>
<td>2.95 ± 0.43</td>
<td></td>
</tr>
<tr>
<td>LHV (MJ/m³)</td>
<td>3.89 ± 0.65</td>
<td>3.64 ± 0.48</td>
<td></td>
</tr>
<tr>
<td>Gas efficiency (%)</td>
<td>34.22 ± 0.43</td>
<td>33.11 ± 0.49</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>For 40%, O₂</th>
<th>Corn cob</th>
<th>Corn stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (%)</td>
<td>8.76 ± 0.22</td>
<td>8.64 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>CO (%)</td>
<td>10.43 ± 0.20</td>
<td>8.82 ± 0.20</td>
<td></td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>4.24 ± 0.09</td>
<td>3.85 ± 0.21</td>
<td></td>
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<tr>
<td>LHV (MJ/m³)</td>
<td>4.65 ± 0.73</td>
<td>4.55 ± 0.71</td>
<td></td>
</tr>
<tr>
<td>Gas efficiency (%)</td>
<td>33.83 ± 0.56</td>
<td>32.75 ± 0.52</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>For 50%, O₂</th>
<th>Corn cob</th>
<th>Corn stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (%)</td>
<td>10.68 ± 0.24</td>
<td>10.52 ± 0.24</td>
<td></td>
</tr>
<tr>
<td>CO (%)</td>
<td>12.45 ± 0.22</td>
<td>11.12 ± 0.22</td>
<td></td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>3.18 ± 0.30</td>
<td>4.54 ± 0.98</td>
<td></td>
</tr>
<tr>
<td>LHV (MJ/m³)</td>
<td>5.84 ± 0.46</td>
<td>5.32 ± 0.40</td>
<td></td>
</tr>
<tr>
<td>Gas efficiency (%)</td>
<td>35.02 ± 0.47</td>
<td>34.94 ± 0.45</td>
<td></td>
</tr>
</tbody>
</table>
The experimental data were statistically analyzed to create regression equations and identify the significant parameters affecting the production. Analysis of variances was used to analyze the model significance by Minitab 17. Generally, the significant terms of the factors are considered by p-value. The p-value less than 0.05 is considered as with statistically significant, and the terms of p-value higher than 0.05 is considered to be insignificant with 95% of confidence level. The insignificant terms were eliminated with no damaging the predictions, the regressions of each response are derived, and shown in Table 2. To visualize the effects of the factors, they were plotted in three-dimensional response surfaces.

3. Results and Discussion

Effect of air, oxygen-enriched air and steam gasification were carried out under various operating conditions of oxygen content (OC: 21, 30, 40, and 50% O₂), equivalence ratio (ER: 0.15, 0.2, 0.25, 0.3, and 0.35) and steam-to-biomass ratio (SB: 0, 0.2, 0.4, 0.6, and 0.8). Both of corn residues behaved in the same trend when the operating conditions are varied. The ranges of the obtained experimental data are shown in Table 3.

3.1 Effect of operating conditions on gas production

The regressions were plotted in 3D surfaces to show the effects of operating relations of OC, ER and SB as shown in Figure 2. Both biomass materials showed similar
The gas production increased with ER and SB, while decreased with OC. Increasing OC had the most impact on gas production, followed by ER and SB, respectively. The increasing of ER increased the amount of air feeding in the system, resulted on the higher gas production. The increased gas was not only from the higher air supply, but also from char decomposition by oxidation, partial oxidation, Boudouard reaction, methanation, and tar cracking. Gas productions at the condition of air gasification with ER of 0.25 were 1.55 and 1.54 Nm/kg for cob and stover. Wongsiriamnuay et al. (2012; 2013) reported a similar range of air gasification from 1.4 to 1.6 Nm/kg using bamboo and mimosa fixed bed gasification.

Gas production was high in air gasification. The use of oxygen enriched air reduced the gas yield. The reduction was mainly from the lower proportion of nitrogen. With the increase of OC, nitrogen was decreased while the amount of the intake oxygen remained the same. The energy for heating the adjacent nitrogen was decreased in a higher OC condition, affecting the approach to obtain faster and higher temperature, tar was cracked into gas phase. However, the tar conversion did not affect the gas production, compared to the decrease in nitrogen.

With introduction of steam, the gas production increased significantly. This can be explained by the fact that the steam reacted with char through water-gas reaction to form H$_2$ and CO gases. Tar was cracked and reformed via steam reforming to enable more gas production. With increasing SB, more steam was available for these reactions and these reactions were favourable at temperature above 800°C (Wei et al., 2007; Lv et al., 2004; Kumar et al., 2009). Using high steam together with high ER in the gasification process, the gas production was less increased, compared to low ER. This was due to the competition of these agents in reacting with char. ER was more reactive than SB. Interaction effect between OC and SB was not significant. Increasing SB in any enriched air gasification increased gas production in similar fashion. The highest gas production was obtained at gasification with ER of 0.35 and SB of 0.8. The lowest was at 50% OC enriched air gasification and ER of 0.15.

3.2 Effect of operating conditions on solid yields

Amount of solid residue from gasification of both materials were significant only by the effects of ER and SB. It was shown that increasing ER and SB decrease the amount of char residue. Increasing ER decreased char residues from around 2.5 to 1.2 g/kg biomass for cob, and from 2.9 to 2.2 g/kg biomass for stover. When more ER was introduced, more oxygen was available to enhance oxidation reactions. The oxidation also produced CO$_2$ that could react with char through Boudouard reaction, resulted in decreased char. Increasing SB at a fixed ER of 0.25 decreased the solid residue from around 1.9 to 1.3 and around 2.4 to 1.9 g/kg biomass for cob and stover, respectively. Increasing SB favoured a reaction in solid carbon and water through water-gas reaction. Methanation was an important reaction that H$_2$ from the process reacted with solid char. However, char decreased faster when ER increased. Similar results were obtained from other reported works.

3.3 Effect of operating conditions on combustible gases

All parameters were significant for combustible gas composition of both materials. Both feedstocks behaved similarly when the process parameters changed. Increasing OC and SB favoured the H$_2$ production, contrasting to increasing ER which decreased H$_2$ production. CO was significantly influenced by OC. Figures 4 to 6 show the plots of the H$_2$, CO, and CH$_4$, respectively. The CH$_4$ contents were generally lower than H$_2$ and CO. They varied in the range between 2 to 9%.

The increase in OC from 21 to 50% was found to increase all combustible gas components. This was because higher OC reduced nitrogen dilution, hence higher concentration of the other gases, including H$_2$, CO,
and CH₄. Some additional H₂ and CO were also expected from tar conversion. However, the increase in CO was higher than the increase in H₂, similar to that reported by Niu et al. (2014). This was due to the strengthened endothermic reactions of Boudouard and water-gas shift at higher OC.

Meanwhile, the H₂, CO, and CH₄ composition were observed to gradually decrease when ER increased from 0.15 to 0.35. All of them decreased at a lower OC condition. Increasing ER boosted the air into the process in which it may dilute the producer gas. The additional oxygen also favoured the oxidation of solid carbon and combustible gases, and reduced partial oxidation in which H₂, CO, and CH₄ were consumed and CO₂ was formed. The increase in ER also reduced durations for gasification reactions. There was the competition for oxygen among different species present in the gasifier: H₂, CO, CH₄, char, tar, etc. It was likely that H₂ and CO reacted with the additional oxygen since they were more reactive species (Fu et al., 2014). However, the oxidations released the heat and the temperature was increased with the amount of ER. High temperature allowed endothermic reactions such as Boudouard, steam reforming, and tar cracking to occur. H₂ and CO were supposed to be generated, but oxidation was more predominant.

H₂ production increased rapidly after introducing steam into the process. The increase was due to increasing reactions between steam with solid carbon, CO and CH₄ by water-gas, water-gas shift and steam reforming. Rupesh et al. (2014) explained that increasing H₂ was mainly due to the effect of exothermic water gas shift reaction. Having steam in low ER conditions appeared to generate more H₂ than at higher ER.

Steam promoted H₂ production, but degraded CO and CH₄ production. The reduction in CH₄ was due to the steam reforming. The CO production increased slightly first and then decreased. This was from the balance of the reactions among water-gas, water-gas shift, and steam reforming. At low SB condition, water-gas and steam reforming reactions were quite effective in increasing CO and H₂. Increasing more steam lowered gasification temperature and the effects of endothermic reactions. The highest H₂ production of 24.15% from cob gasification was achieved at 50% OC, 0.15 ER and 0.8 SB, while 23.9% was for stover gasification at the same condition.

**Fig. 4** Effect of operating conditions on H₂ production in % v/v (shown as Y-axis) from gasification of corn cob (1) and stover (2) at (a) SB = 0.4 (b) ER = 0.25, and (c) OC = 30%
3.4 Effect of operating conditions on LHV

The LHV was calculated based on the proportion of combustible gas contents (H₂, CO, and CH₄). Heat contribution of H₂, CO, and CH₄ are 12.78, 12.71, and 39.76 MJ/m³, respectively. The surface plots are shown in Figure 7. OC had the most significant effect on LHV, followed by ER. The LHV was improved as OC and ER decreased. At ER of 0.25, the LHV from air gasification of corn cob was 4.04 MJ/m³, and stover was 4.21 MJ/m³. Increasing OC to 50% improved LHV to 6.77 MJ/m³ for cob, and 6.94 MJ/m³ for stover. The increases were about 68% and 65%, respectively. The behavior observed can be explained by the analysis of combustible gas composition in Figures 4 to 6. Oxygen enriched air gasification reduced nitrogen dilution and enhanced combustible gas concentration. Low ER produced more concentration of combustible gas in the gas production. LHV increased because steam enhanced the reforming reactions, water-gas, and water-gas shift reaction, and then decreased if excessive. Within the range considered in this study, the highest LHV from cob gasification was 8.08 MJ/m³ at 50% OC, ER of 0.15 and SB of 0.23 and the highest LHV from the stover gasification was 8.17 MJ/m³ at 50% OC, ER of 0.15 and SB of 0.29. It should be noted that the LHV calculated in this work considered only H₂, CO, and CH₄. Other hydrocarbon gases, such as C₂ and C₃, were not measured and considered. The actual LHV of the gas may be slightly higher than the reported here.

Biomass pretreatment by torrefaction may improve gas quality to higher LHV. Although the high LHV was obtained in oxygen enriched air gasification with low ER, the volume of the produced gas was low. The gasification efficiency should be further considered.

Fig. 5 Effect of operating conditions on CO production in % v/v (shown as Y-axis) from gasification of corn cob (1) and stover (2) at (a) SB = 0.4 (b) ER = 0.25, and (c) OC = 30%
3.5 Effect of operating conditions on gasification efficiency

Gasification efficiency is important in considering optimum condition when utilizing this gas for energy. It is defined as the ratio between the energy content of the gas product and the energy content of the biomass input. Increasing OC in enriched air was not found to be significant to the gasification efficiency. Although the higher OC led to higher LHV, the gas production was lower. This observation was similar to Zheng et al. (2016) who reported bio-oil gasification using air, enriched air and oxygen as gasifying agents. Nam et al. (2016) used daily manure as feedstock in a fluidized bed gasifier and reported insignificance of oxygen concentration on gasification efficiency.

Breaking down and partially oxidation of the biomass, tar and other intermediate products led to higher gas yield and an increase in gasification efficiency when ER was increased. However, using excessive air resulted in higher degree of oxidation of the combustible product gases (H₂, CO, and CH₄), hence, the efficiency was degraded.

SB seemed to be the most significant factor affecting the gasification efficiency, as it was increased with increasing SB. Similar agreement was reported by Wang et al. (2007) and Kumar et al. (2009), in which it was expected that the excess steam would decrease gasification temperature. Appropriate amount of steam would increase the efficiency. Within the range considered, the highest gasification efficiencies were 39.4% for cob at the condition of ER = 0.27 and SB = 0.57, and 42.82% for stover at ER = 0.21 and SB = 0.8. Although the use of higher oxygen concentration in enriched air gasification did not significantly affect gasification efficiency, lower nitrogen dilution led to higher burning temperature which was useful for the high temperature heating systems (Sittisun and Tippayawong, 2019; Punnarapong et al., 2017).

Fig 6 Effect of operating conditions on CH₄ production in % v/v (shown as Y-axis) from gasification of corn cob (1) and stover (2) at (a) SB = 0.4 (b) ER = 0.25, and (c) OC = 30%
4. Conclusion

Gasification of corn cob and stover using oxygen-enriched air and steam mixtures as gasifying medium has been studied. Effects of oxygen enrichment from 21 to 50%, equivalence ratio between 0.15 and 0.35, and steam to biomass ratio from 0 to 0.8 were investigated. Both types of feedstock materials behaved in similar ways. The use of oxygen enriched air reduced the nitrogen dilution effect. Increasing oxygen was observed to increase combustible gas (H$_2$, CO, and CH$_4$) proportion and LHV. Changing air gasification to 50% OC gasification, LHV was improved from 4.04 to 6.77 MJ/m$^3$ for cob, and 4.21 to 6.94 MJ/m$^3$ for stover, respectively. An increase in equivalence ratio increased gas yields, but decreased combustible gas components and LHV of the producer gas.

Applying steam was observed to favor mainly H$_2$ production, whereas CO and CH$_4$ production was decreased. LHV and gasification efficiency was found to initially increased, and then decreased at higher amount of steam. The highest LHV from cob gasification was 8.08 MJ/m$^3$ at 50% OC, ER of 0.15 and SB of 0.23, while the highest LHV from stover gasification was 8.17 MJ/m$^3$ at 50% OC, ER of 0.15 and SB of 0.29. The highest gasification efficiency was 39.44% at ER of 0.27 and SB of 0.58 for cob gasification, and 42.82% at ER of 0.21 and SB of 0.8 for stover gasification.

![Fig. 7 Effect of operating conditions on LHV in MJ/m$^3$ (shown as Y-axis) from gasification of corn cob (1) and stover (2) at (a) SB = 0.4 (b) ER = 0.25, and (c) OC = 30%](image-url)
Fig 8 Effect of operating conditions on efficiency in % (shown as Y-axis) from gasification of corn cob (1) and stover (2)

Acknowledgments

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References


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