OPEN ACCESS

2nd World Sustainability Forum
1-30 November 2012

www. wsforum.org

Article

Effect of Temperature and Steam to Biomass Ratio on NO and SO_2 Production in Palm Kernel Shell Catalytic Steam Gasification with In-situ CO_2 Adsorption

Zakir Khan[1], Suzana Yusup[1,*] and Murni Melati Ahmad[1]

[1] Department of Chemical Engineering, University Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak , Malaysia

E-Mails: khan.zakir@gmail.com; drsuzana_yusuf@petronas.com.my; murnim@petronas.com.my
* drsuzana_yusuf@petronas.com.my, Tel.: +60-53687642/3688208;
Fax: +60-5- 3656176

Received:

Abstract: The emission of NO_x and SO_x has been received considerable attention in last few decades due to the severe associated problems such as acid rain which has harmful effect on aquatic ecosystem, plant and infrastructure. Biomass contains less sulphur and nitrogen content and thus threat to environment is less compared to coal. Power plants using biomass combustion and co firing of biomass with coal are of great concerned in the recent years to generate electricity. Therefore, the present study highlights the emission of NO and SO_2 from gasification of local biomass feedstock i.e. palm kernel shell using catalyst and steam with in situ CO_2 adsorbent in a pilot scale fluidized bed gasification system. The effect of two important variables i.e. temperature and steam to biomass are investigated. Temperature is varied from 600°C to 750°C while steam to biomass ratio is varied in the range of 1.5 to 2.5 (wt/wt). The lower reactor temperature (600°C) contributes to the lower concentration of NO and SO_2 i.e. <70 ppm and <120 ppm, respectively, at steam to biomass ratio of 2.0, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1. By increasing steam to biomass ratio from 1.5 to 2.5, the NO and SO_2 formations are decreased, and reached the minimum concentration of 20 ppm and 100 ppm, respectively, at temperature of 675 °C, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1. The results are then discussed and compared with commercial biomass power plants.

Keywords: NO_x and SO_x, CO_2 adsorption, Palm oil wastes, Catalytic steam gasification

---

1. Introduction

Emissions of NO_x and SO_x causes environmental problem such as acid rain. NO_x and SO_x are produced from inherent sulfur and nitrogen contents in biomass and their formation from the thermal treatment of biomass can be determined based on the fraction of sulfur and nitrogen obtained in ultimate analysis. Nitrogen in biomass is oxidized during the combustion/gasification of biomass processes in to NO. If the excess oxygen is available (especially in case of combustion), NO is further oxidized into NO_2. Similarly, SO_2 reacts with oxygen to produce SO_2. The formation of NO_x and SO_x are significant in coal combustion/gasification due to its high sulfur and nitrogen content [1]. However, power plants using biomass combustion suffer from these types of emissions and proper emission controls techniques are followed. Unlike combustion, biomass gasification produces low NO_x and SO_x since the degradation take place in limited oxygen supply [2].

Limited studies have been reported for the NO_x and SO_x in biomass gasification system. Patel et al. (2001) [3] studied the gasification based biomass co-firing utilizing poultry litter in commercial updraft fixed bed gasifier. NO and SO_2 concentrations of 477 ppm and 193 ppm, respectively, were observed at the gasifier temperature of 843°C. Dayton et al. (2002) [4] reviewed the NO_x reduction from co-firing of biomass with coal by varying proportion of sawdust and wheat straw in the commercial scale fluidized bed systems. They reported that the NO_x reduction has linear relationship with biomass proportion. Miles et al. (2005) [5] studied the removal of NO_x and SO_x from the combustion of mixture of swine solid and turkey litter using CaO in pilot scale fluidized bed combustor. They reported NO_x and SO_x in the range of 10-50 ppm and 0-25 ppm at temperature of 720°C. Sethuraman et al. (2010) [6] studied the concentration of NO_x emission from gasification wood and corn using different nitrogen content in pilot scale fluidized bed system. The NO_x concentration of 215 ppm and 600 ppm were reported for wood and corn, respectively, at temperature of 815°C and equivalence ratio of 0.15.

Most of the works reported are based on the combustion/gasification of solid waste of animal manure and specific type of biomass. Moreover, the processes were carried out at high temperature. Biomass steam gasification in the presence of catalyst and/or CO_2 adsorbent is a potential way to produce syngas and hydrogen rich product gas for power generation. Palm oil wastes which are abundantly available in Malaysia can be a renewable source to produce high value gas of power generation. For the sake of environmental monitoring, the toxic emissions i.e. NO_x and SO_x need to be kept in the certain level to avoid any environmental problem such as acid rain. Therefore, the present study is carried out to investigate the effect of temperature and steam to biomass ratio on NO and SO_2 in the product gas from catalytic steam gasification of palm kernel shell (PKS) with in-situ CO_2 adsorption.

2. Methodology

2.1 Biomass sample

Palm kernel shell (PKS), type of palm oil wastes was used as feedstock in this study. The grinded PKS with diameter range of 0.1-4 mm was supplied by My 4-Seasons International Sdn. Bhd. The biomass waste was then sieved to particle size of 1.0-2.0 mm. The palm kernel shell has been characterized in accordance with the procedure of American Society for Testing and Materials (ASTM) to assure their potential as feedstock for H_2 production through gasification process and the basic properties are summarized in Table 1.

Table 1. Palm kernel analysis

Analysis	wt % (dry basis)
Moisture	9.61
Volatiles	80.92
Ash	4.31
Fixed Carbon (by diff.)	14.67
C	49.74
H	5.68
N	1.02
S	0.27

2.2 Catalyst and bed material preparation

Ni powder (99 % Ni) was used as the catalyst in the present study which was supplied by Merck Chemicals. The particle diameter of Ni powder was in the range of ~10 μm.

Quicklime was used as a bed material as well as the source of CaO to adsorb CO_2 in the product gas and was purchased from Universal Lime Sdn. Bhd., Malaysia. The sample was grinded and sieved to particle size of 150-250 μm. The physical properties of the catalyst and bed material are given in Table 2.

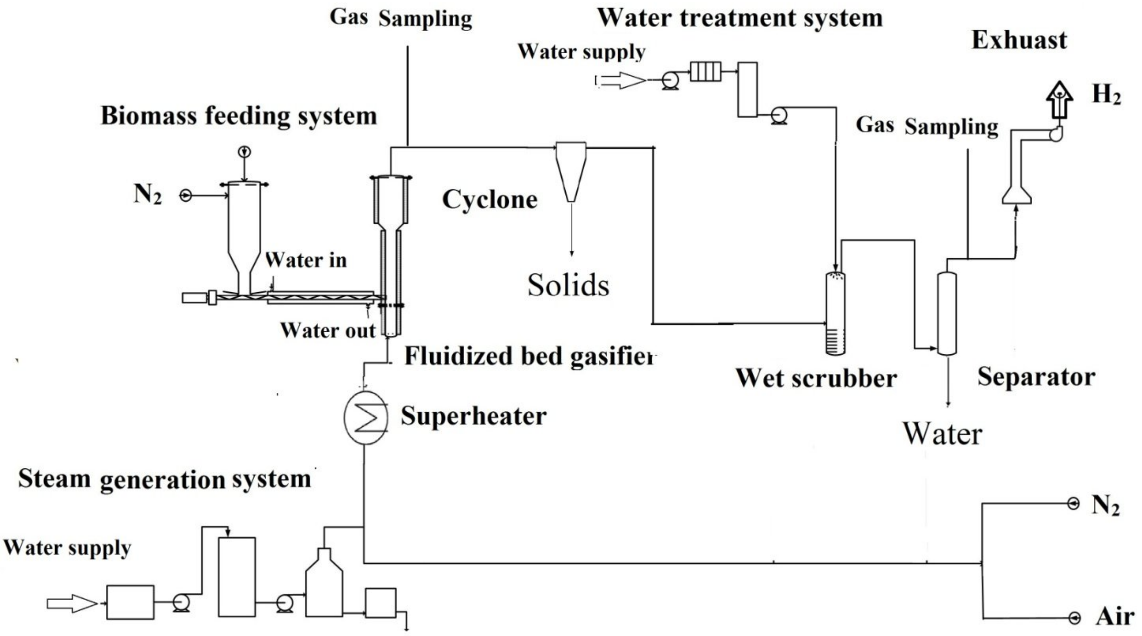
Table 2. Catalyst and bed material properties

Properties	Value
Bed material (Quicklime)	
Particle diameter (μm)	150-250
Particle density (kg/m^3)	3053
Bulk density (kg/m^3)	1047
Ni catalyst	
Particle diameter (μm)	10

2.3 Experimental apparatus and procedure

The experiments for catalytic steam gasification of PKS with in-situ CO_2 adsorption were performed in a pilot scale fluidized bed gasifier shown in the Figure 1. The main reactor system consisted of externally heated fluidized bed gasifier of 0.15 m internal diameter and height of 2.5 m, continuously fed from the side of the biomass feeding system. The cooling water jacket was provided to the feeding system to avoid biomass decomposition in the feeding line prior injection to the gasifier. The feeding point was located 0.30 m above the distributor plate. N_2 was used to purge the biomass into the gasifier to avoid any back flow. The main gasifier is equipped with 4 external and 3 internal thermocouples to monitor the gasifier temperature at different locations. The three internal temperature measuring points were located at i) bottom (before the distributor ii) middle (above the distributor) and iii) top (in the freeboard). Saturated steam was provided by a 6 bar boiler system which was further heated to 300°C in superheater prior injection to the gasifier. A cyclone with the particle cut off diameter of 50 µm was used to separate the solid particles from the product gas. The product gas was then passed through to the wet scrubber to cool down the product gas temperature less than to 40°C, followed by a separator to remove the final traces of water in the product gas stream. Product gas was analyzed at the exit of the separator.

Figure 1. Experimental set up for pilot scale fluidized bed steam gasification system



The bed material was first introduced into the fluidized bed gasifier which was then heated up to the desired temperature. At this stage, N_2 gas was purged into the system to remove entrapped gases. Afterwards, superheated steam was injected into the gasifier from the superheater when the temperature inside the gasifier became stable. Catalyst was mixed with the biomass for all runs performed. The continuous feeding of PKS and catalyst mixture was started when the temperature of the system was stable at the desired reactor temperature. After the gasifier, the product gas was passed through the cyclone to separate solid particles from the product gas. The NO and SO_2 were analyzed using Teledyne's Series 7600 gas analyzer. All experimental runs lasted for 60 min. This time is chosen due to the completion of the gasification process which takes at least 50 min in the fluidized bed gasifier [7].

Table 3. Experimental operating conditions

Parameter	Value
Biomass feed rate (kg/hr)	1.1-1.8
Steam flow rate (kg/hr)	2.70
Steam to biomass ratio (wt/wt)	1.0, 1.5, 2.5
Catalyst to biomass ratio (wt/wt)	0.1
Adsorbent to biomass ratio (wt/wt)	1.0
Gas (steam) superficial velocity (m/s)	0.21
Reactor temperature (°C)	600, 675,750
Pressure (atm)	1

3. Results and Discussions

3.1 Effect of temperature

In the present study, the effect of temperature on NO and SO_2 formation is studied for palm kernel shell catalytic steam gasification with CO_2 adsorbent. Figures 2 and 3 provide the NO and SO_2 profiles, respectively, at temperature of 600°C, 675°C and 750°C. The NO concentration in the product gas is presented in ppm (parts per million). The profiles clearly show that the temperature has significant effect on the NO concentration. At temperature of 600°C and 675°C, the NO concentration in the product gas is less than 100 ppm. At 750°C, the concentration is increased to 10 times of the concentration at lower temperature. These trends match with those reported on biomass and coal gasification plants presented in the literature [8]. Low temperature in gasification can reduce NO_x emissions.

Figure 2. NO profiles at 600°C, 675°C and 750°C (steam to biomass ratio of 2.0, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1)

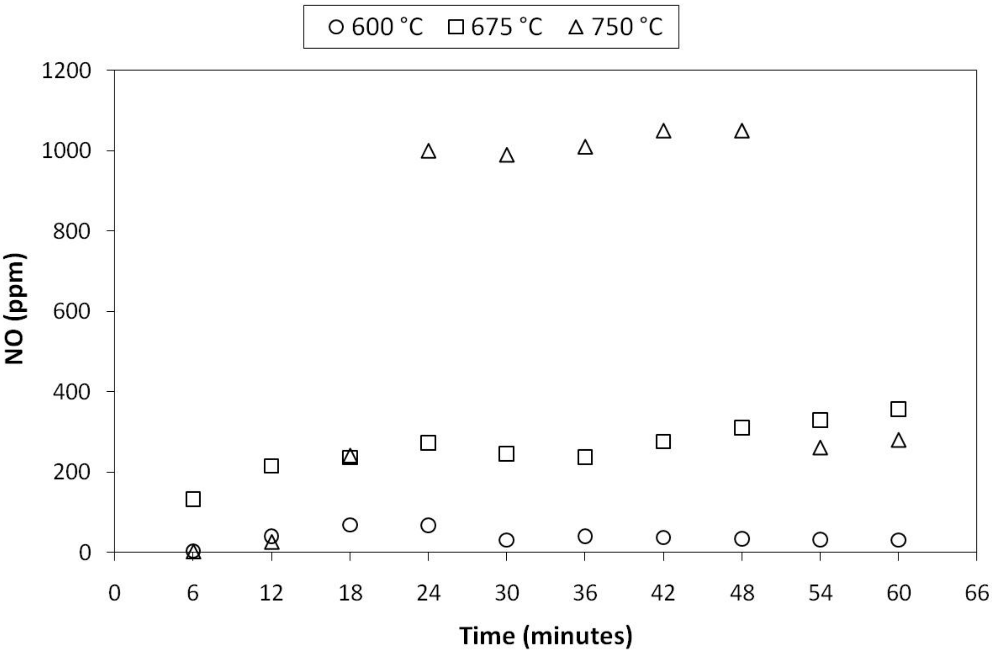
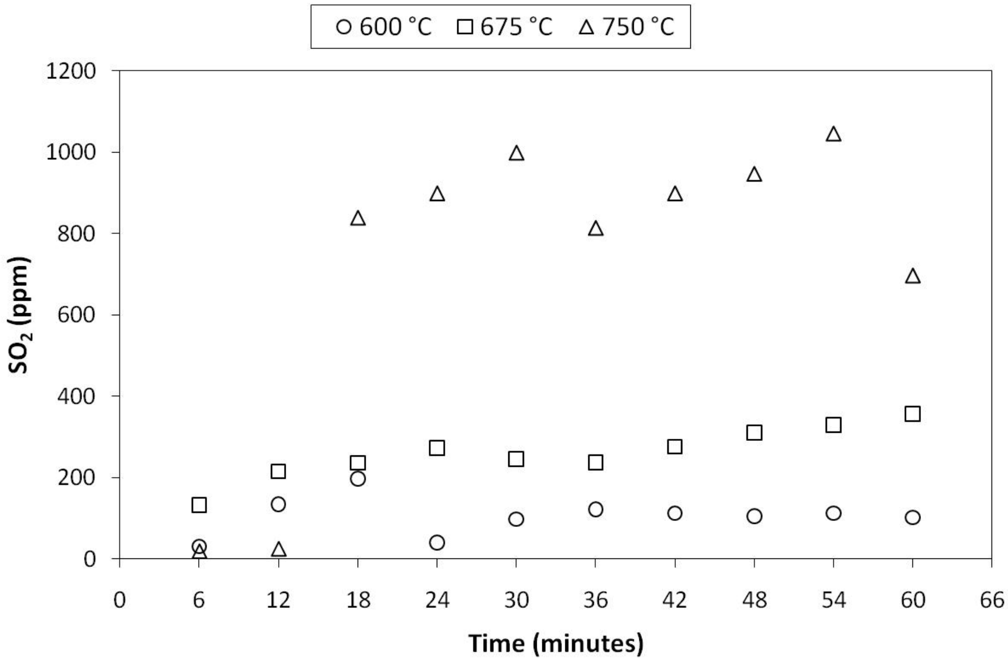


Figure 3 represents SO_2 profiles with respect to time at 600°C, 675°C and 750°C. The concentration at 600 °C varies between 30 ppm to 200 ppm which is then reached to 100 ppm. At temperature of 675 °C, this concentration first increased and then decreased up to less than 400 pm. The use of CaO based adsorbent to enhance SO_2 removal is well supported by a number of studies [9-12]. Additionally, at high temperature of 750°C, SO_2 emission profiles follows almost similar trend with that of NO and reached concentration in the range of 800-1000 ppm.

Figure 3. SO_2 profiles at 600°C, 675°C and 750°C (steam to biomass ratio of 2.0, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1)



3.2 Effect of steam to biomass ratio

The effect of steam to biomass (S/B) ratio on NO and SO_2 generation is shown in Figures 4 and 5. The experiments were operated at three different level of S/B ratio i.e. 1.5, 2.0 and 2.5 at constant temperature of 675 °C, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1. All ratios are presented in wt/wt basis.

Figure 4 shows the variation in NO formation with respect to S/B ratio. Initially, For S/B of 1.5, the NO formation reached to highest value of 119 ppm at 12 minute of gasification process which is the maximum values observed amongst the entire range of S/B. After 12 minutes, the NO concentration is gradually decreasing to a lowest value of 30 ppm. Similarly, at S/B of 2.0, the NO generated is the second highest at 18 minutes of gasification process and reached a value of 69 ppm, and then attained the steady state value of 31 ppm. Steam injection depletes and the environment inside the system becomes oxygen deficient thus helps to reduce the NO content in product gas. The reduction of NO values occurred after 12 and 18 minutes of gasification processes at 1.5 and 2.0 S/B. Conversely, at S/B ratio of 2.5, NO profiles are different. The NO contents started at low concentration of 10 ppm and then attained the value of 23 ppm. The different NO concentration profiles at different S/B may be due to the different amount of steam introduced in fluidized bed gasifier at different S/B ratio. This can be justified by the order of the maximum NO concentration at the start (12-36 minute) of gasification process for different S/B ratio are 119(1.5) > 69(2.0) > 44 (2.5). These results are supported by the literature [13].

Figure 4. NO profiles at steam to biomass ratio of 1.5, 2.0, 2.5 (temperature of 675 °C, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1)

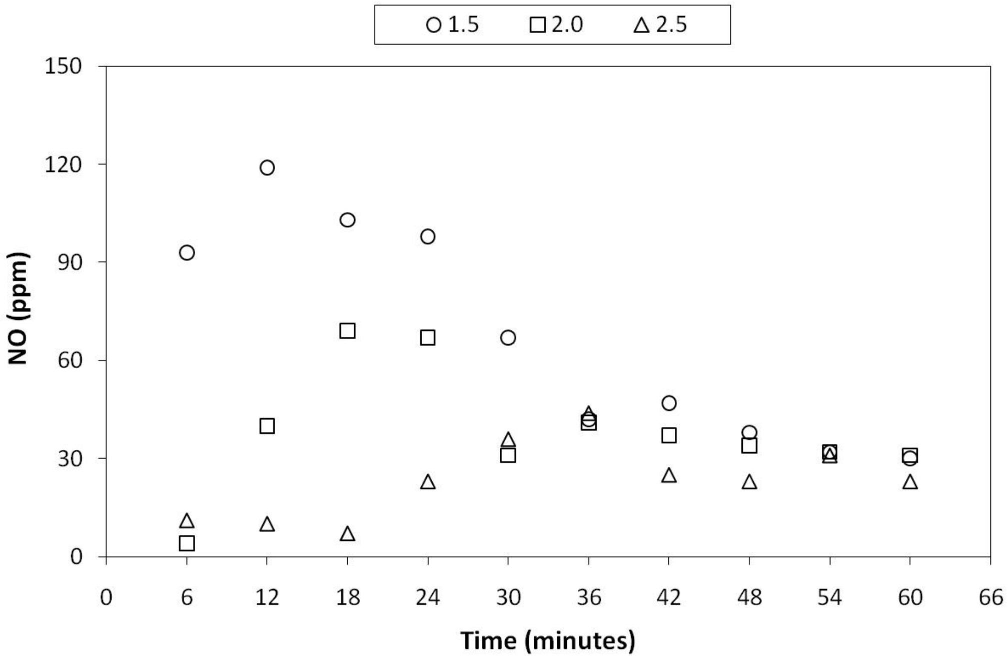
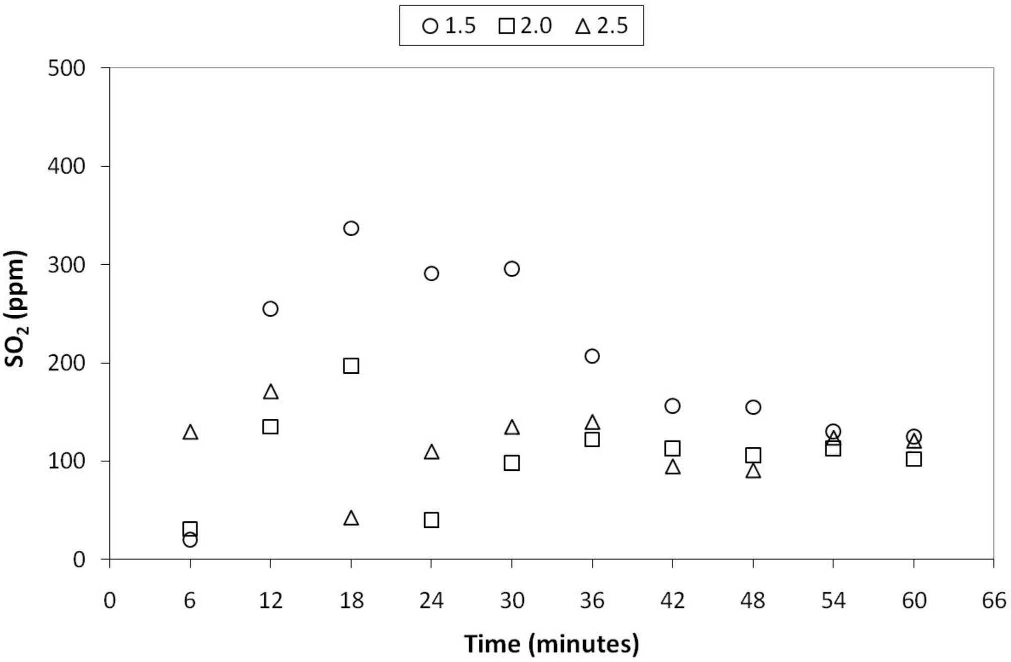


Figure 5 describes the effect of S/B ratio of 1.5, 2.0 and 2.5 on SO_2 composition in the product gas. The profiles are similar to those observed for NO generation. SO_2 content decreased with increasing S/B ratio from 1.5 to 2.5. At 1.5, maximum SO_2 generation reached is around 300 ppm at 18 minute of gasification process and then decreased to steady value of 125 ppm. Likewise, at 2.0 S/B, the value generated is first reached to maximum value of 197 ppm at 18 minute and then decreased to a stable value of 113 ppm. SO_2 profile for S/B ratio of 2.5 exhibits similar trend as observed in NO and reached to 120 ppm. Moreover, in the first 30 minutes, there is significance difference in the concentration of NO and SO_2 at different S/B ratio. After this, difference in concentration is gradually decreased up to 60 minutes for S/B ratio of 1.5, 2.0 and 2.5. Consequently, almost similar concentration of NO and SO_2 is observed at high reaction time (>30 minutes) for all S/B ratios i.e. 1.5, 2.0 and 2.5. With time, the incoming steam in the fluidized bed gasifier swept out the oxygen content which generate oxygen deficient environment. This can be justified with lower SO_2 concentration at time higher than 42 minutes of the gasification process.

Based on the observation, low temperature and high steam to biomass ratio in the presence of CO_2 adsorbent reduced considerably NO and SO_2 emissions from catalytic steam gasification of PKS. The aim of the results presented here is to provide the basic study on NO_X and SO_x formation in biomass steam gasification which is not reported in the literature. The less interest of NO_x and SO_x study in the subject area may be due to low sulfur and nitrogen content present in biomass.

Figure 5. SO_2 profiles at steam to biomass ratio of 1.5, 2.0, 2.5 (temperature of 675°C, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1)



3.3 Comparative study

The comparative study for NO and SO_2 emission from some biomass gasification processes are provided in Table 4. In the present study, the minimum concentration of the NO and SO_2 observed are 30 ppm and 110 ppm, respectively, at temperature 600°C, S/B ratio of 2.0, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1. Study performed by Sethuraman et al. (2010) reported NO concentration of 215 ppm using wood as the feedstock in an air gasification process. No SO_2 data is available for the system as the study focused only NO_x formation in the product gas. As shown in Table 4, the present study provides comparable proportions of NO and SO_2 in the product gas when compared with pilot and commercial scale systems. NO formation in our study is closer to the values provided by the MTCI (Manufacturing and Technological Conversion International) system which may be due to similar gasification agent and small temperature difference between two gasification processes. All other studies were operated at high temperature (>815°C) and consequently give high NO formation. Similar observations were also found to be true for SO_2 concentration. Study [3] operated at much high temperature of 1300-1400°C and eventually emitted highest NO and SO_2 formation in the product gas.

Table 6 shows the comparison of the NO and SO_2 concentration with the present Air Quality Standard (AQS) in Malaysia [14]. The challenge is to reduce the emissions of these gases to meet the standard requirement.

Table 4. Comparative study on NO and SO_2 formation

Parameters	Current study	Sethuramanet al. (2010) [6]	Ciferno et al. (2002) [1]		Patel et al. (2001) [3]
Reactor	FB[a]	FB[a]	FB[a] (MTCI)[b]	FB[a] (Sorfresid)[c]	FixB[d]
Biomass	Palm kernel shell	Wood	Pulp sludge	Municipal solid waste	Wood
Gasification agent	Steam	Air	Steam	Air	Steam
Temperature (°C)	675	815	790-815	1300-1400	843
Pressure (atm)	1	1	1	1	1
Steam/biomass (wt/wt)	2.5	NA	-	-	-
Adsorbent/biomass (wt/wt)	1	1	-	-	-
Catalyst/biomass (wt/wt)	0.1	NA	NA	NA	NA
N content (wt%)	1.02	0.14	-	2.3	3.75
S content (wt%)	0.27		-	0.3	0.64
NO (ppm)	30	215	25	120	477
SO_2 (ppm)	110	NA	9[e]	79[e]	193

[a]Fluidized bed, [b]Manufacturing and technological conversion international, [c]Sorfresid/caliqua technologies, [d] Fixed bed , [e]SO_x, “-“ shows unknown or not reported, [NA] not applicable

Table 5. Comparative study with Air Quality Standard (AQS) in Malaysia

Component	Present study	Malaysian AQS [14]
NO (ppm)	30	0.17
SOx (ppm)	110	0.13

4. Conclusion

The increasing energy demand from biomass sources is of concern and monitor of hazardous emission particularly NO and SO_2 in the product gas is important. The present study reports the findings obtained from when investigating the effect of the basic process variables i.e. temperature and steam to biomass ratio on NO and SO_2 formation in catalytic steam gasification of PKS with in-situ CO_2 adsorption in a pilot scale fluidized bed gasification system. The studied has shown that low gasification temperature and high steam to biomass ratio helped to reduce NO and SO_2 concentration in the product gas. The future work will further investigate the effect of two more process variables i.e. adsorbent to biomass ratio and biomass particle size on NO and SO_2 production in catalytic steam gasification of PKS with in-situ CO_2 adsorption.

Acknowledgement

The authors gratefully thank the Universiti Teknologi PETRONAS for the financial support.

References

1. J.P. Ciferno; Marano, J. J. *Benchmarking biomass gasification technologies for fuels, chemicals and hydrogen production*; U.S. Department of Energy, National Energy Technology Laboratory: 2002.
2. Chapter7, Biomass Power Plants In *San Joaquin Valley Unified Air Pollution Control District*, 2010.
3. Patel, B. *Gasifcation based biomass co-firing*; Department of Energy, USA,: 2001.
4. Dayton, D. *A summary of* NO_x *emissions reduction from biomass cofiring*; National Renewable Energy Laboratory, US Department of Energy: Colorado 2002.
5. T.R Miles; Bock, B. R. In *Energy and nutrient recovery from combustion of swin solids and turkey litter* Animal Waste Management Symposium, , 5- 7 October, North Carolina, USA, 2005; 5- 7 October, North Carolina, USA, 2005.
6. Sethuraman, S. Performance of a pilot scale biomass gasification and producer gas combustion system using feed stock with controlled nitrogen content. Iowa State University, Ames, 2010.
7. Basu, P.; Kaushal, P., Modeling of pyrolysis and gasification of biomass in fluidized beds: A review. *Chemical Product and Process Modeling* **2009,** *4*, A 21.
8. Jay A. Ratafia-Brown; L. M. Manfredo; J. W. Hoffmann, M. R.; Stiegel, G. J., An environmental assessment of IGCC power systems. In *19th Annual Pittsburgh Coal Conference* Pittsburgh, USA, 2002.
9. Khan, W. Z.; Gibbs, B. M., SO_X emissions from a fluidized-bed combustor with and without limestone addition. *Energy* **1996,** *21*, 105-113.
10. Khan, W. Z.; Gibbs, B. M., Reduction of SO_2 emissions from a fluidized bed under staged combustion by fine limestone. *Environment International* **1997,** *23*, 227-236.
11. C. H. Nelli; Rochelle, G. T., Simultaneous sulfur dioxide and nitrogen dioxide removal by calcium hydroxide and calcium silicate solids. *Air & Waste Management Association* **1998,** *48*, 819-828.
12. S. V. Loo *Biomass combustion and Co-firing: An Overview*; International Energy Agency: 2002.
13. R. Pavri; Moore, G. D. *Gas turbine emissions and control*; General Electric Energy Services,: 2001.
14. Development, A.; Bank *Country synthesis report on Urban air quality mangament: Malaysia* 2006.