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Effect of Temperature and Steam to Biomass Ratio on NO and SO₂ Formation in Palm Kernel Shell Catalytic Steam Gasification with In-situ CO₂ Adsorption

Zakir Khan¹, Suzana Yusup^{1,*} and Murni Melati Ahmad¹

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

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Abstract: The emissions of NO_x and SO_x has been given considerable attention in last few decades due to the severe associated problems such as acid rain which has harmful effect on aquatic animal life, plant and infrastructure. The topic is more concerned in coal combustion/gasification which contains high sulphur and nitrogen content. 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 emissions of NO and SO₂ from local biomass feedstock i.e. palm kernel shell under catalytic steam gasification with in situ CO₂ adsorbent in pilot scale fluidized bed gasification system. Two important variables i.e. temperature and steam to biomass are considered. 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 SO₂ 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 SO₂ formation is decreased, and achieved 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, CO₂ adsorption, Palm oil wastes, catalytic steam gasification

1. Introduction

Emissions of NO_x and SO_x causes problem such as acid rain to the environment. NO_x and SO_x are produced from inherent sulfur and nitrogen content in biomass and their composition are determined in the process are based on the fraction of sulfur and nitrogen presence in ultimate analysis. Nitrogen in biomass is oxidized during the combustion/gasification of coal/biomass processes into 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_3 . 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, are observed at the gasifier temperature of 843 °C. Dayton et al. (2002) reviewed the NO_x reduction from co-firing of biomass with coal by varying different proportion of biomass in the commercial scale fluidized bed systems. They reported that the NO_x reduction has linear relationship with biomass proportion. Miles et al. (2005) [4] 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) [5] studied the concentration of NO_x emission utilizing biomass feedstock with different nitrogen content such as wood and corn in pilot scale fluidized bed gasification system. The NO_x concentration of 215 ppm and 600 ppm are reported for wood and corn, respectively, at temperature of 815 °C and equivalence ratio of 0.15.

It can be concluded that most of the work reported are based on the combustion/gasification of the solid waste of animal manure. Moreover, the processes are carried out at high temperature. Biomass steam gasification in the presence of catalyst or CO_2 adsorbent is a potential way to produce syngas and hydrogen rich product gas for the energy application. 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 utilizing palm kernel shell catalytic steam gasification with in situ CO_2 adsorption.

2. Methodology

2.1 Biomass sample

Palm kernel shell (PKS) is used as a palm oil wastes in this study. The grinded PKS, 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 H₂ production through gasification process and the basic properties are summarized as 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 is in the range of ~10 µm.

Quick lime was used as a bed material as well as the source of CaO to adsorb CO₂ in the product gas and was obtained from Universal Lime Sdn. Bhd. 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 the Table 2.

Table 2. Catalyst and bed material properties

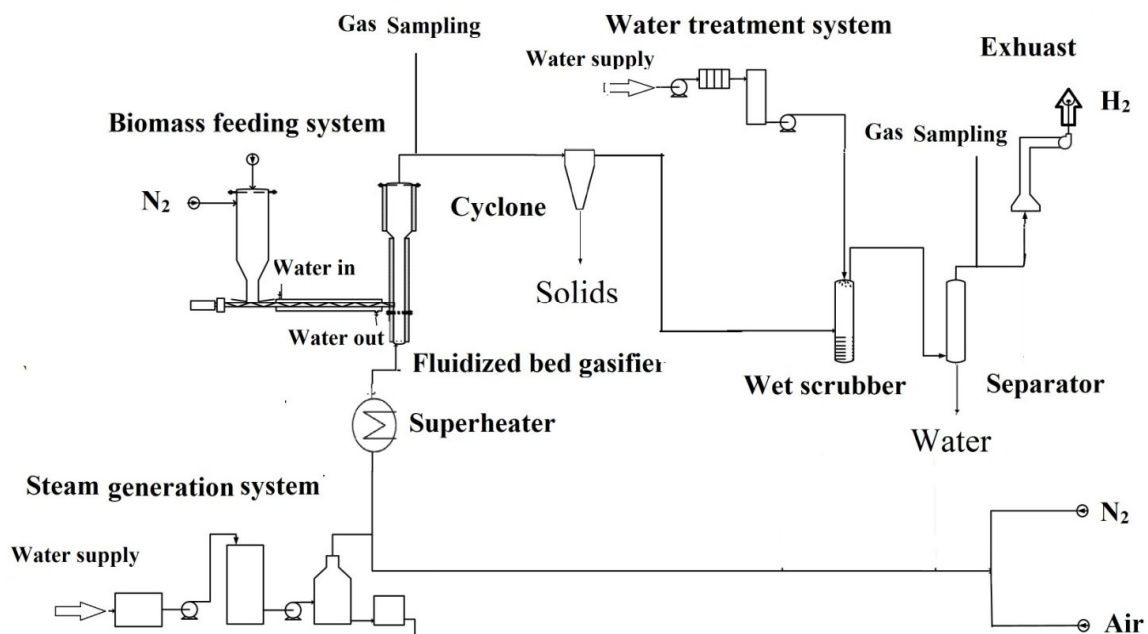
Properties	Value
<i>Bed material (Quicklime)</i>	
Particle diameter	150-250 µm
Particle density	3053 kg/m ³
Bulk density	1047 kg/m ³
<i>Ni catalyst</i>	
Particle diameter	10 µm

2.3 Experimental apparatus and procedure

The palm kernel shell catalyst steam gasification with in situ CO₂ adsorption experiments were performed in a bench scale system as 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. The gasifier was followed by a cyclone (cut off diameter of 50 μm) 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 up to < 40 °C, followed by a separator to remove the final traces of water in the product gas stream. Two gas sampling points were provided which were located after the fluidized bed gasifier and separator. In the present study, 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 biomass feeding started when the temperature of the system was stable to 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.

Table 3. Experimental operating conditions

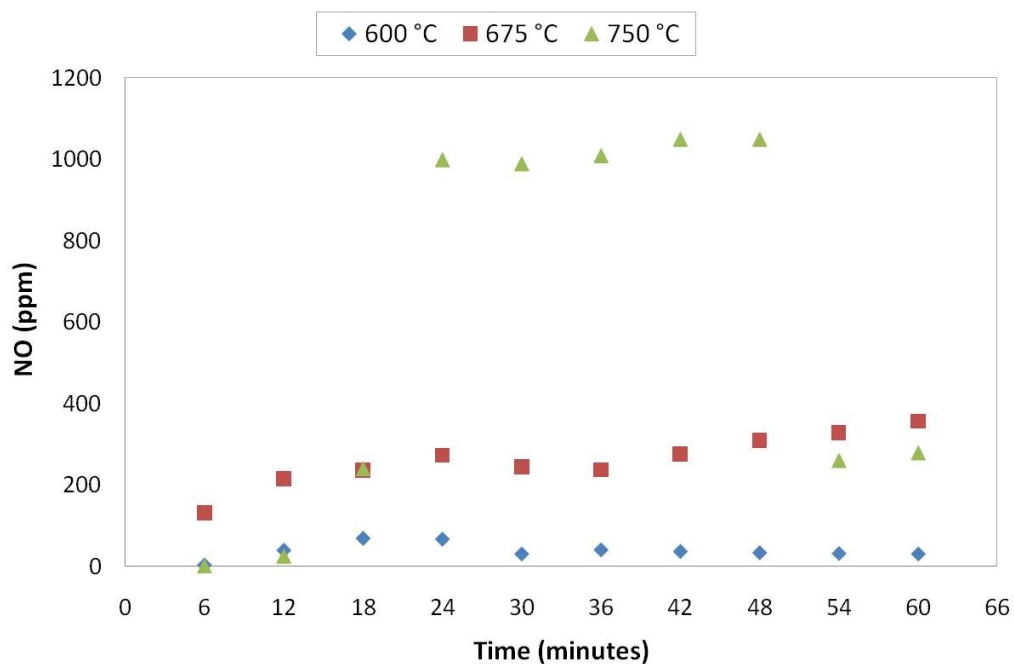
Parameter	Value
Biomass feed rate	1.35 kg/hr
Steam flow rate	2.70 kg/h
Steam to biomass ratio	1.0, 1.5, 2.5
Catalyst to biomass ratio	0.1 (wt/wt)
Adsorbent to biomass ratio	1.0 (wt/wt)
Gas (steam) superficial velocity	0.21 m/s
Reactor temperature	600 °C, 675 °C 750 °C
Pressure	1 atm

3. Results and Discussions

3.1 Effect of temperature

In the present study, effect of temperature on NO and SO₂ formation is studied for palm kernel shell catalytic steam gasification with CO₂ adsorbent. Figures 2 and 3 provide the NO, SO₂ profiles 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

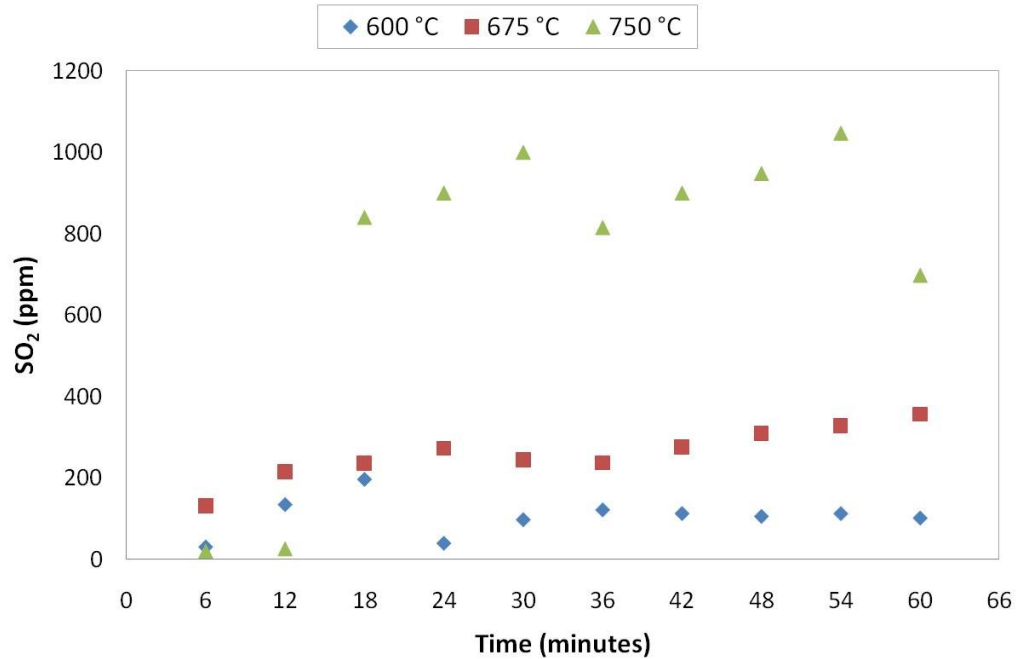
Figure 2. NO profiles at 600 °C, 675 °C and 750 °C (steam to biomass ratio of 2.0; adsorbent to biomass ratio of 1.0, catalyst to biomass ratio of 0.1)



temperature. These results are well supported by the biomass and coal gasification plants presented in the literature where low temperature is implemented to reduce NO_x emissions [6].

Figure 3 represents SO₂ 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 become steady state at 100 ppm. At temperature of 675 °C, this concentration is first increased and then decreased up to less than 400 ppm. The use of CaO based adsorbent to enhance SO₂ removal is well supported by a number of studies [7-10]. Additionally, at high temperature of 750 °C, SO₂ emission follows almost similar trend as NO and attained concentration in the range of 800-1000 ppm.

Figure 3. SO₂ profiles at 600 °C, 675 °C and 750 °C (steam to biomass ratio of 2.0; adsorbent to biomass ratio of 1.0, 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 SO₂ generation is shown in Figure 4 and 5. The experiments are operated at three different level of S/B ratio of 1.5, 2.0 and 2.5 at 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 the first 24 minute of gasification process, the values are at their maximum for S/B ratio of 1.5 and 2.0 and then gradually decreasing to a lowest value of 30 ppm. For 1.5 ratio, the NO formation reached to highest value of 119 ppm which is the maximum values observed amongst the entire range of S/B. Similarly, at 2.0, the NO generated is the second highest and reached a value of 69 ppm, and then reached to 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 24 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.

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, catalyst to biomass ratio of 0.1)

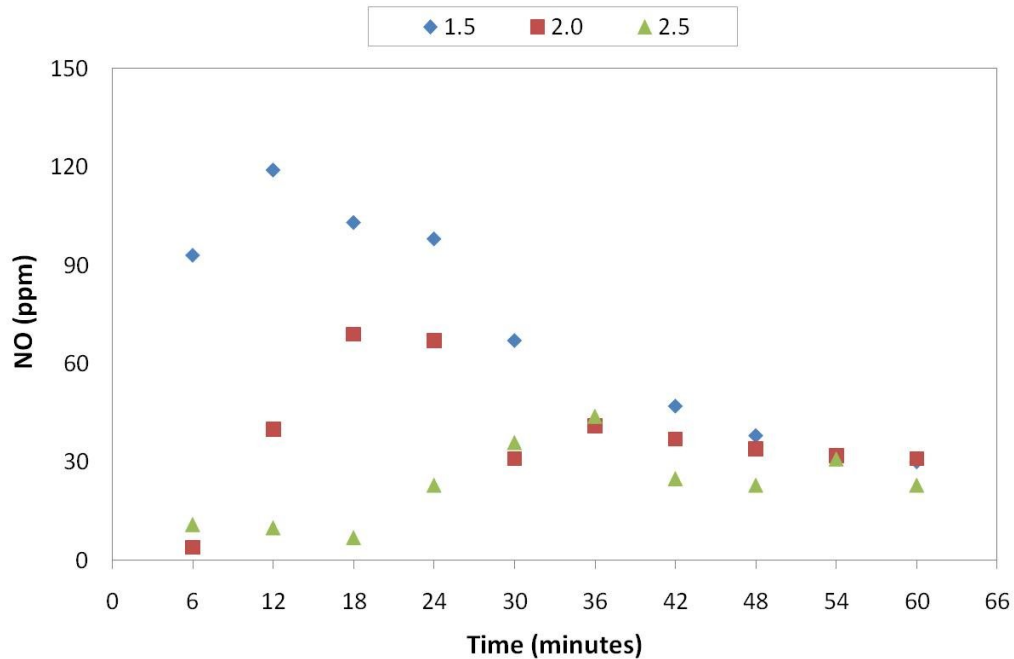
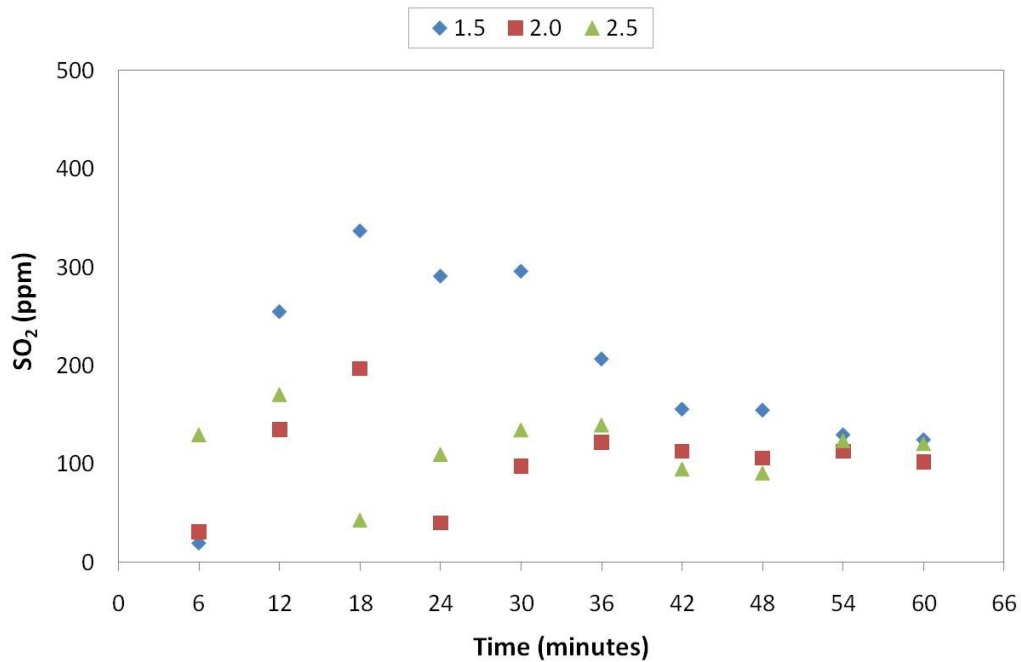


Figure 5 describes the effect of S/B ratio of 1.5, 2.0 and 2.5 on SO_2 composition in the product gas. The profiles are similar to those observed in NO generation. SO_2 content decreased with increasing S/B ratio from 1.5 to 2.5. At 1.5, maximum SO_2 generation reached is around 300 ppm and then decreased to 125 ppm. Likewise, at 2.0 S/B, the values generated is first increased, and then decreased. It increased to steady values of around 110 pm. SO_2 profile for S/B ratio of 2.5 exhibits similar trend as NO and reached to 120 ppm. However, similar trends are observed for S/B of 2.0 and 2.5. 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. With time, the incoming steam in the fluidized bed gasifier swept out the oxygen content which generate oxygen deficient environment. 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.

Based on the discussions, low temperature and high steam to biomass ratio in the presence of CO_2 adsorbent reduced considerable NO and SO_2 emissions in palm kernel shell catalytic steam gasification. The amount of NO and SO_2 emissions are not so much critical in the present operating conditions where high steam flow rates produce a reduction in the amount of NO and SO_2 to the environment due to the oxygen deficiency in the presence of adsorbent material; which inhibits the said pollutant emissions. However, 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. SO₂ profiles at steam to biomass ratio of 1.5, 2.0, 2.5 (temperature of 675 °C; adsorbent to biomass ratio of 1.0, catalyst to biomass ratio of 0.1)



3.3 Comparative study

The comparative study for NO and SO₂ concentration is provided in Table 4. In the present study, the minimum concentration of the NO and SO₂ 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) produced NO concentration of 215 ppm using wood as the feedstock under air gasification environment. No SO₂ data is available for the system as the study focused only NO_x formation in the product gas. The gasification system comprised of a fluidized bed gasifier and currently operates in Bio-energy Conversion (BECON), Nevada, Iowa state, USA. The system represented by MTCI (Manufacturing and Technological Conversion International) is utilizing pulp sludge as feedstock and operated under steam environment. The gasification system provided by Solfresid (Coliqua technologies) is operated at high temperature (1300-1400 °C) as compared to other system.

As shown in Table 4, the present study provides comparable proportions of NO and SO₂ in the product gas when compared with pilot and commercial scale systems. NO formation is closer to the values provided by the MTCI system which is may be due to similar gasification agent and less temperature difference between two gasification processes. All other studies are operated at high temperature (>815 °C) and give high NO formation. Similar observations are also found to be true for SO₂ concentration. Study [3] operated at much high temperature of 1300-1400 °C and eventually emits highest NO and SO₂ formation in the product gas.

Table 6 shows the comparison of the NO and SO₂ concentration with the present Air Quality Standard (AQS) in Malaysia [11]. The challenge is to reduce the emissions of these gases to meet the standard requirement.

Table 4. Comparative study of NO and SO₂ formation

Parameters	Current study	Sethuramanet al. (2010) [5]	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

^aFluidized bed, ^bManufacturing and technological conversion international, ^cSorfresid/caliqua technologies, ^dFixed bed, ^eSO_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 [11]
NO (ppm)	30	0.17
SO _x (ppm)	110	0.13

4. Conclusion

NO_x and SO_x have been recognized as basic source of acid rain in the environmental pollution. Alternative energy sources such as biomass are recognized as one of the potential source of renewable energy. The increasing energy demand from biomass sources is of concern and monitor of hazardous emission particularly NO and SO₂ in the product gas is important. The present study is an attempt to provide the effect of the basic process variables i.e. temperature and steam to biomass ratio on NO and SO₂ formation in palm kernel shell catalytic steam gasification with in situ CO₂ adsorption in 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 SO₂ concentration to the minimal level in the product gas.

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