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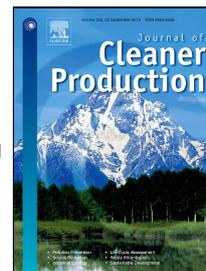
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# Accepted Manuscript

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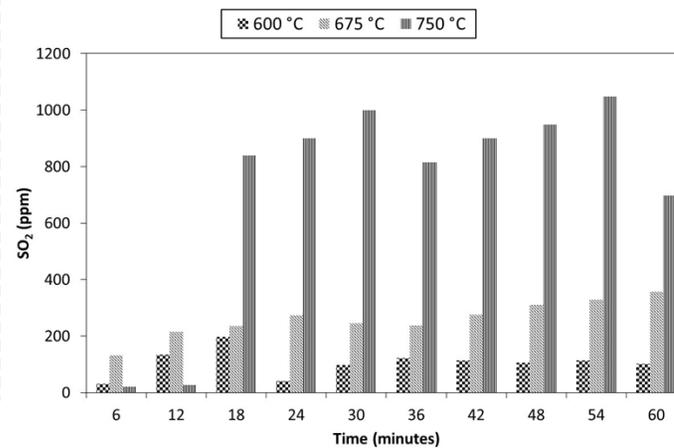
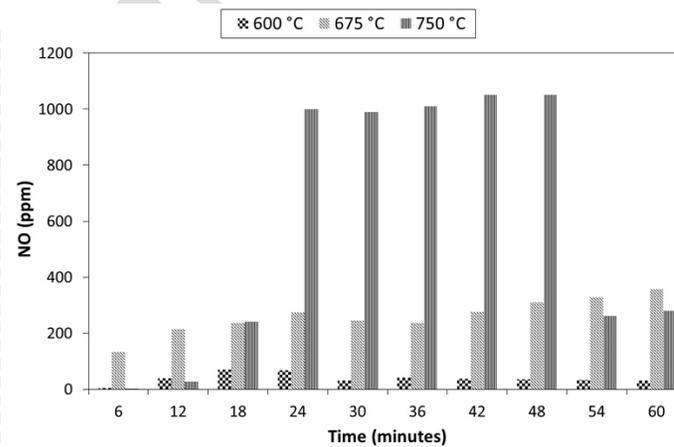
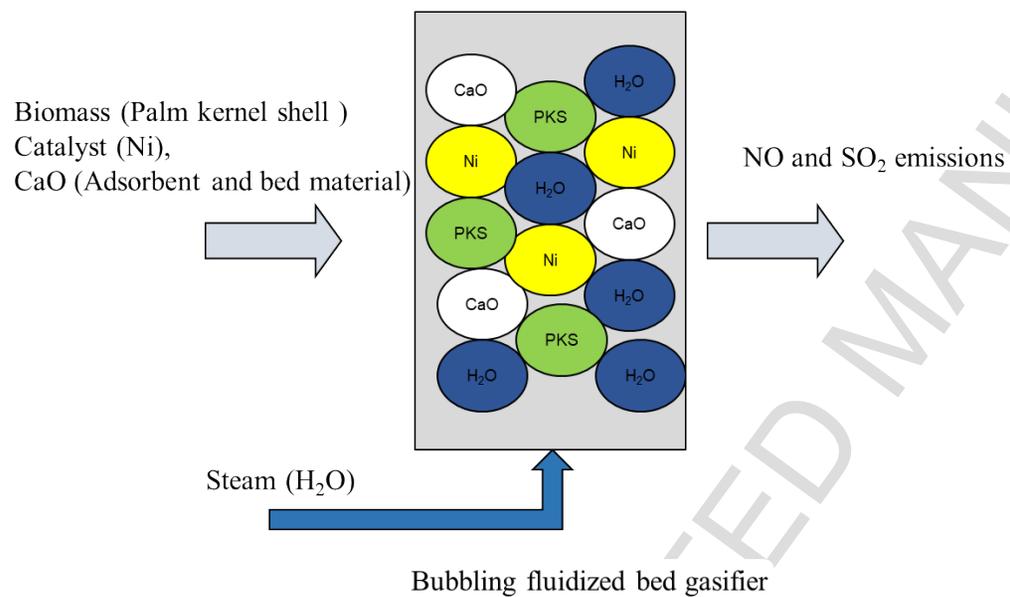
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## Graphical Abstract



Words count=5327, Paragraphs=173, Lines=500

**NO and SO<sub>2</sub> emissions in palm kernel shell catalytic steam gasification with in-situ CO<sub>2</sub> adsorption for hydrogen production in a pilot-scale fluidized bed gasification system**

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## Abstract

The NO and SO<sub>2</sub> emissions in enhanced hydrogen production from palm kernel shell (PKS) steam gasification with integrated catalytic adsorption steam gasification is investigated. The influence of steam and adsorbent to biomass ratios (1.5-2.5, 1.0-1.5), temperature (600-750°C), biomass particle size (0.355-2.0 mm) and fluidization velocity (0.15-26 m/s) was reported. The results inferred that lower temperature (600°C) contributed to emissions of NO (30 ppm) and SO<sub>2</sub> (110 ppm) whereas high steam to biomass ratio (2.5 wt/wt) produced the emissions of <30 ppm and <110 ppm, respectively, at experimental conditions of 675°C, adsorbent to biomass ratio of 1.0 (wt/wt) and catalyst to biomass ratio of 0.1 (wt/wt). The lowest average minimum NO and SO<sub>2</sub> concentration of 16 ppm and 46 ppm, respectively, was observed at 675°C, steam to biomass ratio of 2.0 (wt/wt), adsorbent to biomass ratio of 1.5 (wt/wt) and catalyst to biomass ratio of 0.1(wt/wt). Nevertheless, fluidization velocities were proportional to the emissions and small particle size (0.3-0.5 mm) contributed to high NO and SO<sub>2</sub>. The comparative studies found that the present study produced similar emission of NO (30 ppm) when compared with commercial indirect heated fluidized bed gasifier using steam as oxidizing agent. Besides, some other studies operated at high temperature reported high NO and SO<sub>2</sub> concentration which might be due to the temperature as the most influential variable in the context.

**Keywords:** NO<sub>x</sub> and SO<sub>x</sub>, CO<sub>2</sub> adsorption, Oil palm wastes, Catalytic steam gasification, Hydrogen production

## 1. Introduction

The worldwide economic development and industrialization have accelerated the emissions of NO<sub>x</sub>, SO<sub>x</sub> and other greenhouse gases; and their associated harmful effects on global warming and other environmental problems (Baleta et al., 2019). Recently, several technologies such as membrane processes (Saqib et al., 2019), nitrifying-enriched activated sludge (NAS) (Sepehri and Sarrafzadeh, 2018), adsorption (Pan et al., 2017), absorption (Kouravand and Kermani, 2018) etc. have been reported to reduce or capture greenhouse gases. Numerous works are reported for releasing of CO<sub>2</sub> emissions and

capturing in thermochemical conversion process (Burmistrz et al., 2016; Fan et al., 2019). In coal gasification, the release of  $\text{NO}_x$  and  $\text{SO}_x$  are equally important as like  $\text{CO}_2$  due to large quantity of S and N in coal (Li and Fan, 2016). Nitrogen and sulfur also present in biomass feedstock are oxidized into NO and  $\text{SO}_2$  during gasification/combustion processes (J.P. Ciferno and Marano, 2002). Although combustion is very important for energy production, but it emits large amount of  $\text{NO}_x$  and  $\text{SO}_x$  (Zhao et al., 2016). Unlike combustion, gasification of biomass generates low  $\text{NO}_x$  and  $\text{SO}_x$  due to limited supply of oxygen available (Suopajarvi et al., 2017).

$\text{NO}_x$  formation can be categorized into thermal  $\text{NO}_x$ , fuel  $\text{NO}_x$  and prompt  $\text{NO}_x$ . Thermal  $\text{NO}_x$  releases at high temperature ( $>1300^\circ\text{C}$ ) and the formation is controlled by molar concentration of nitrogen and oxygen. Fuel  $\text{NO}_x$  formation links to the oxidation of inherent nitrogen content in biomass (Shah et al., 2018). Prompt  $\text{NO}_x$  formation is related to nitrogen in air and fuel in fuel rich conditions. Based on the temperature ranges ( $600\text{--}750^\circ\text{C}$ ) considered in the present study, fuel  $\text{NO}_x$  may be sole responsible to generate  $\text{NO}_x$  from integrated catalytic adsorption (ICA) steam gasification.

There are a few studies reported on emissions of  $\text{NO}_x$  and  $\text{SO}_x$ . For co-combustion, Moron et al. (Moroń and Rybak, 2015) investigated the  $\text{NO}_x$  and  $\text{SO}_2$  formation in biomass-coal blend in oxy-air-combustion atmosphere at higher temperature ( $1000^\circ\text{C}$ ). The studied found that the mixing of both fuels reduced the  $\text{NO}_x$  and  $\text{SO}_2$  emissions. Yanik et al. (Yanik et al., 2018) studied the emissions of  $\text{NO}_x$  and  $\text{SO}_x$  and sintering effect for co-combustion of biomass-coal blended at  $800^\circ\text{C}$  and  $900^\circ\text{C}$ . For gasification and co-gasification, Patel et al. (Patel, 2001) reported generation of NO and  $\text{SO}_2$  during gasification of biomass with co-firing of poultry litter using commercial-scale fixed-bed gasification system. The NO and  $\text{SO}_2$  reported were 193 and 477 ppm, respectively, at constant temperature of  $843^\circ\text{C}$ . Some other researchers (Sethuraman, 2010) studied the emissions of  $\text{NO}_x$  from gasification of corn and wood to evaluate the impact of different contents of nitrogen in pilot-scaled fluidized-bed gasification system. The concentrations of  $\text{NO}_x$  were found to be 600 and 215 ppm from gasification of corn and wood, respectively, at  $815^\circ\text{C}$  and equivalence ratio of 0.15. Chen et al. (Chen et al., 2018) reported the formation of  $\text{NO}_x$  for pyrolysis and co-gasification of corn straw and sewage sludge in tubular furnace

reactor. It was observed the formation of  $\text{NO}_x$  is highly affected by heating rate,  $\text{H}_2/\text{N}_2$  ratio, synergy effect of biomass and mixing of sludge with biomass in pyrolysis. In addition, Shahyan et al. (Shayan et al., 2018) investigated the formation of  $\text{NO}$  and  $\text{SO}_2$  for gasification of wood and paper for  $\text{H}_2$  hydrogen using four different oxidizing agent i.e. air,  $\text{O}_2$ -air, steam, air-steam. However,  $\text{NO}$  and  $\text{SO}_2$  generation was only reported for wood and municipal solid wastes. Recently, Ahmad et al. (Ahmed et al., 2019) reported less  $\text{NO}_x$  emissions generation in small scale biomass gasification system than open burning biomass. However, further improvements in downstream cleaning system were proposed when large scale biomass gasification system is considered for power generation (Ahmed et al., 2019). It can be concluded that most of the studies for  $\text{NO}_x$  and  $\text{SO}_x$  emissions have been carried out for combustion, gasification, co-combustion and co-gasification of biomass and coal mainly air and oxygen as an oxidant where  $\text{NO}_x$  and  $\text{SO}_x$  generation using steam as a sole oxidant for biomass gasification with catalyst or  $\text{CO}_2$  adsorption has not been investigated.

Oil palm wastes are available abundant in Malaysia and can be utilized as a renewable resource for power generation and value-added bioproducts. Malaysia and Indonesia are largest producer of oil palm worldwide and collectively produced 12.8 Mt of PKS in 2015 (Khan et al., 2018a). The better physical properties among other oil palm wastes i.e. high calorific value, high fixed carbon, volatile matter, and low ash and moisture content makes PKS has a potential feedstock for hydrogen production through gasification (Abdullah and Yusup, 2010). Some extensive research has been conducted for  $\text{CO}_2$  capturing for palm kernel shell as a feed stock for hydrogen rich gas production through steam gasification (Shahbaz et al., 2017; Yusup et al., 2014). However, emission of  $\text{NO}_x$  and  $\text{SO}_x$  would be worth investigating for renewable hydrogen production from potential biomass wastes such as palm kernel shell through steam gasification.

To date,  $\text{NO}_x$  and  $\text{SO}_x$  emissions have been extensively studied for combustion/gasification or co-combustion/co-gasification using air/ $\text{O}_2$  as an oxidant. Most of these studies focused only one or two parameters i.e. temperature and fuel mixing for  $\text{NO}_x$  and  $\text{SO}_x$  emissions. Other process parameters i.e. steam to biomass ratio, adsorbent to biomass, particle size and fluidization velocity which are not

reported to date and will be important to study for NO<sub>x</sub> and SO<sub>x</sub> emission. Nevertheless, steam gasification of biomass has a potential process to produce H<sub>2</sub> rich gas and widely integrated with CO<sub>2</sub> capturing as well as with catalyst to enhance the H<sub>2</sub> concentration and yield. The present study is considered to evaluate the influence of temperature, steam to biomass ratio, adsorbent and steam to biomass ratios, fluidization velocity and particle size of biomass on NO and SO<sub>2</sub> emission in catalytic steam gasification of PKS integrated with *in-situ* CO<sub>2</sub> adsorption for hydrogen production in a pilot-scaled fluidized bed system. The study is further compared with the commercial gasification plants and local (Malaysian) Air Quality Standards (AQS).

## 2. Materials and methods

### 2.1 Feedstock

PKS is used for this study which is obtained from oil palm industry. PKS is extracted through screw process from palm oil fruits in palm oil process. Palm oil fruit first subjected to washed and sterilized through steam at temperature of 140°C. The sterilized fruit bunches send to rotary drum to separate fruit from bunches through threshing process. The fruit passed through digestion and screw process that separate the oil from solid materials. The solid material passed through cyclone and nut cracker to separate the palm pressed fibers (PPF) and PKS (Bakar et al., 2018; Embrandiri et al., 2013; Prasertsan et al., 1996). The particle size of the PKS as received was 0.1- 4.0 mm. The particle size was sieved to 0.355-5.0 mm and 1.0-2.0 mm. The physical properties of PKS are listed in Table 1.

**Table 1.** Properties of palm kernel shell (PKS) (Yusup et al., 2014)

Properties	Value
Moisture (wt. %)	9.61
Proximate analysis (wt. %)	
Volatile matter	81.03
Fixed carbon	14.87
Ash contents	4.10
Ultimate analysis (wt. %)	

Carbon	44.61
Hydrogen	5.58
Nitrogen	0.46
Sulphur	0.11
Oxygen (by difference)	49.24
Calorific value (MJ/kg)	
HHV	17.32

## 2.2 Bed material and catalyst

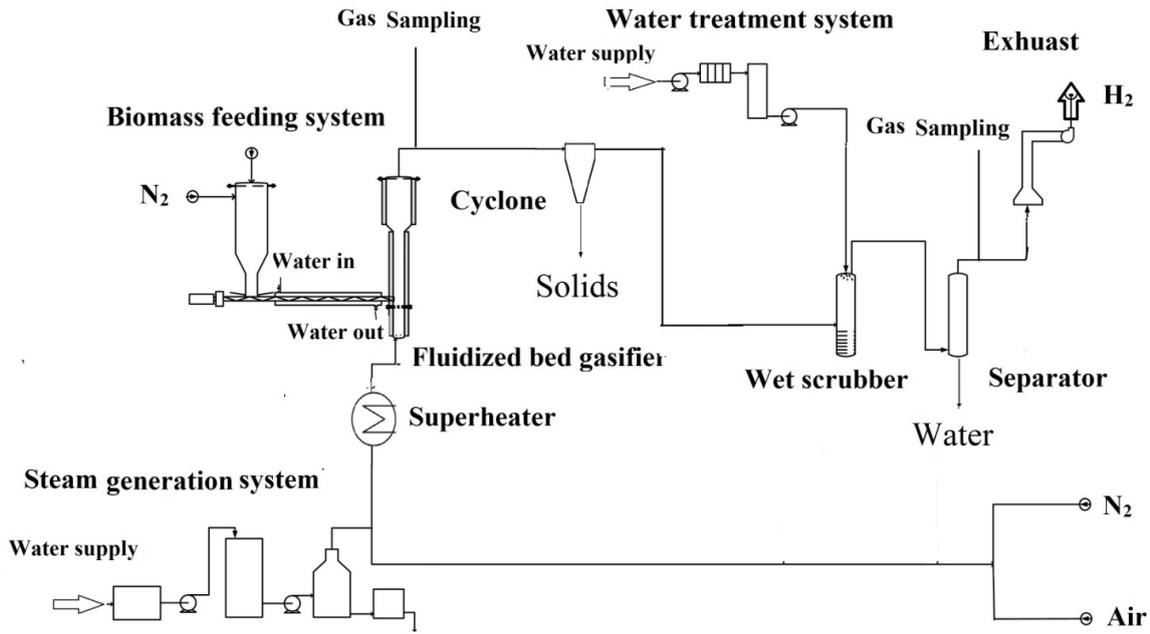
The quicklime (CaO) performed a dual role of bed particle as well as a source of CO<sub>2</sub> capturing in the bed. CaO was supplied by Universal Lime Sdn. Bhd., Malaysia. The bed material was crushed and sieved to a particle size of 150-250  $\mu\text{m}$ . Besides, Ni (99 % purity) was used as catalyst with the particle size of  $\sim 10$   $\mu\text{m}$ . The catalyst was supplied by Merck KGaA, Germany. The physical properties of bed material are listed in Table 2.

**Table 2.** Characteristics of bed material (CaO) (Khan et al., 2014a)

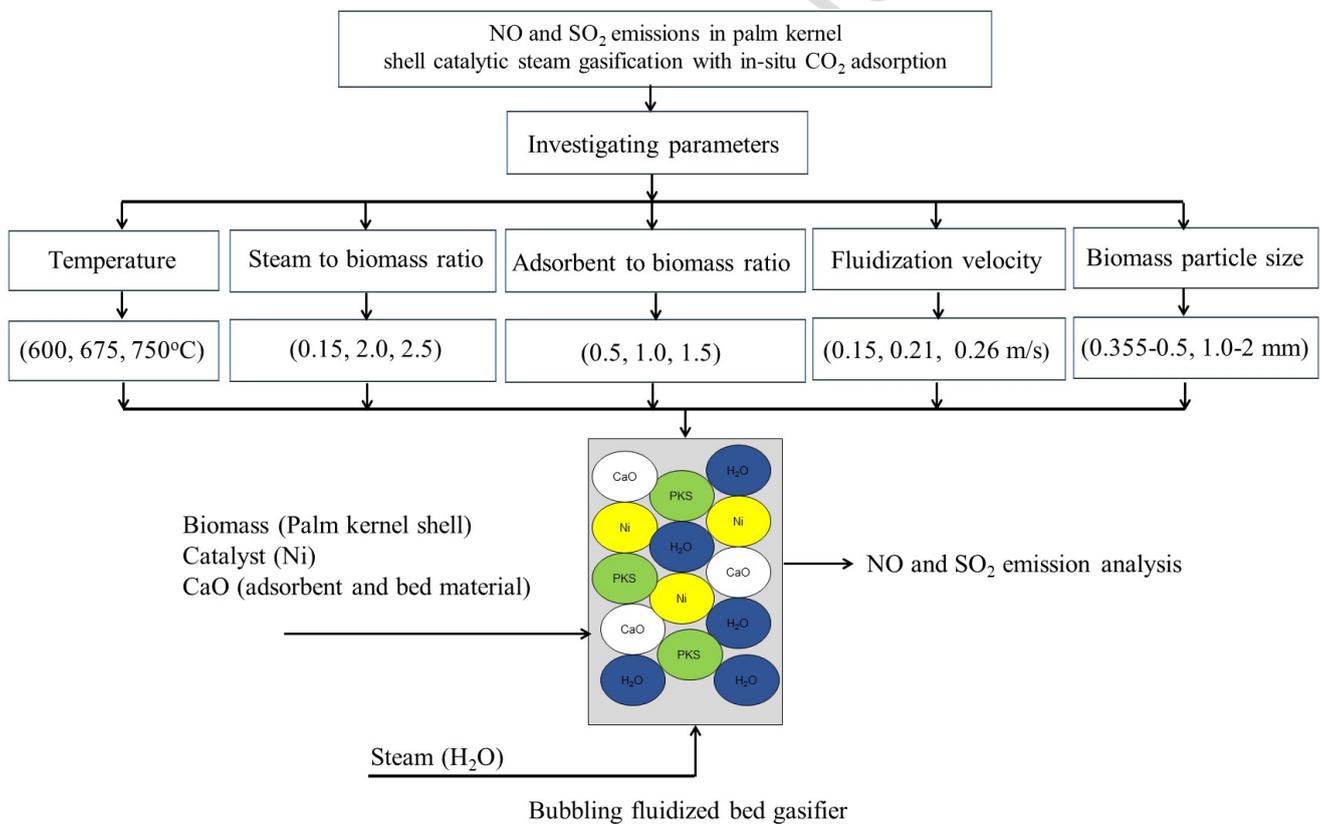
Properties	Value
Particle density (kg/m <sup>3</sup> )	3053
Bulk density (kg/m <sup>3</sup> )	1047
Chemical Composition (wt%)	
Calcium oxide (CaO)	93.32
Magnesium oxide (MgO)	4.24
Silicon dioxide (SiO <sub>2</sub> )	0.95
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	0.23
MnO, CuO, SrO, ZnO),	1.0

## 2.2 Experimental apparatus and procedure

The integrated catalytic-adsorption (ICA) steam gasification of PKS was investigated in a pilot scale fluidized bed system as shown in Fig. 1 (a) whereas Fig. 1 (b) shows the investigating parameters chart. The system mainly comprised of an externally heated fluidized bed reactor with 0.15 m ID and 2.5 m height. The reactor system was assisted by biomass feeder and steam generation system (mainly consisted of boiler and superheater). The feeding line was located some 0.30 m above from the distributor plate and contained water jacket to evade decomposition of biomass in the feed line. The injection of biomass into the gasifier was assisted by N<sub>2</sub> purging. Three thermocouples (standard error  $\pm 1\%$ ) were installed; below the distributor plat, in the bed and above the bed (freeboard) to monitor the temperature distribution of the gasifier. Steam at 6 bars and 300 °C was injected to the gasifier. At the exit of the gasifier, solid particles were removed from product gas using a cyclone with 50  $\mu\text{m}$  as a cutoff diameter. The product gas was then passed through to the wet scrubber to cool down its temperature  $< 40^\circ\text{C}$ . The final traces of moisture in the product gas were removed in the separator prior injection to the gas analyzing system. The NO and SO<sub>2</sub> measurements were carried out via Teledyne's Series 7600 gas analyzer (standard error  $\pm 0.5\%$ ). The time of each experiment was set to 60 min which is well supported by the study (Basu and Kaushal, 2009) for completion of gasification process.



(a)



(b)

**Fig. 1** Pilot scale gasification system (a) schematic and (b) investigating parameters chart

**Table 3.** Experimental operating conditions

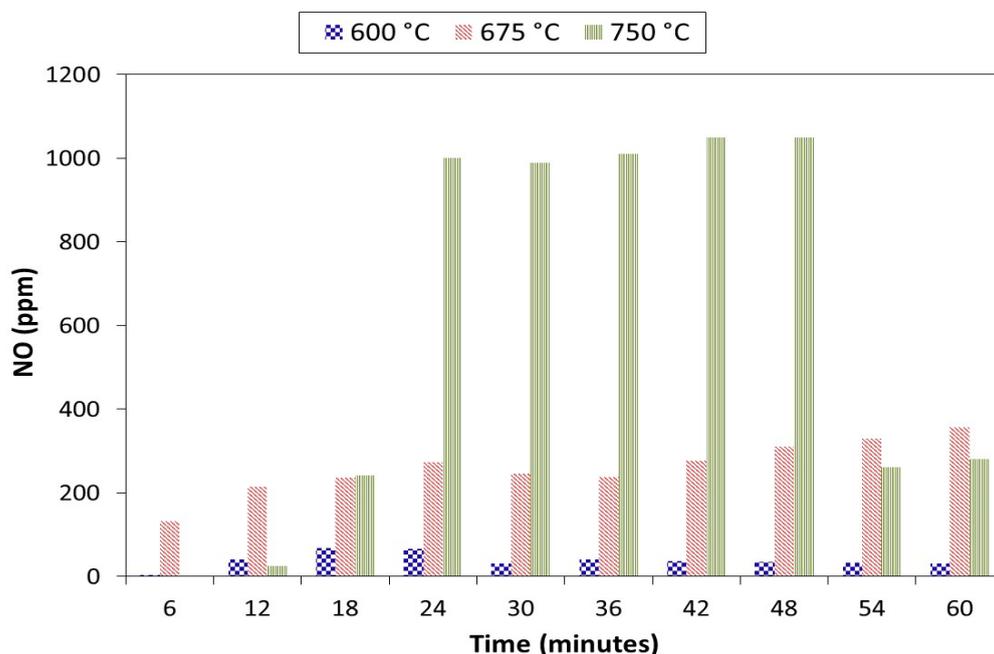
Variable	Range
Biomass (kg/h)	1.1-1.8
Steam (kg/h)	2.0-3.4
Steam to biomass (wt/wt)	1.0, 1.5, 2.5
Adsorbent to biomass (wt/wt)	0.5, 1.0, 1.5
Superficial velocity (m/s)	0.15 (3 $U_{mf}$ ), 0.21 (4 $U_{mf}$ ), 0.26 (5 $U_{mf}$ )
Biomass particle size (mm)	0.355-0.50, 1.0-2.0
Catalyst to biomass (wt/wt)	0.1
Gasification temperature (°C)	600, 675, 750
Pressure (bar)	1.0

### 3. Results and Discussions

#### 3.1 Effect of temperature

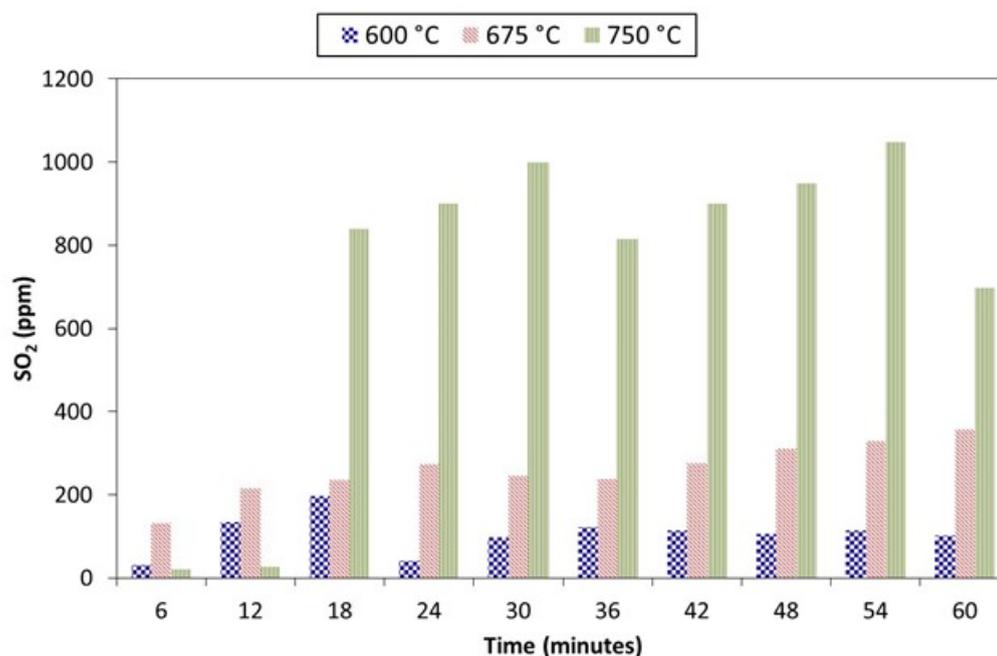
The effect of variable temperature on NO and SO<sub>2</sub> generation was investigated for 600, 675 and 750°C. NO and SO<sub>2</sub> profiles with respect to temperature were shown in Fig. 2 and 3. The results clearly reveal that temperature has a significant impact on NO and SO<sub>2</sub> formation in PKS catalytic gasification integrated with *in-situ* CO<sub>2</sub> adsorption.

The minimum NO concentration of <30 ppm was observed at 600°C whereas this concentration climbed up to 200 ppm when temperature increased to 675°C. Likewise, the NO concentration at 750°C increased 5 times as compare to values observed at 675°C. The continuous increase of NO concentration with respect to temperature was widely observed in gasification and combustion plants utilizing biomass and coal as a feedstock. This infers that biomass gasification at low temperature can significantly reduce NO emissions in the environment. (Khan et al., 2012).



**Fig. 2.** NO concentration with variable temperature at steam to biomass ratio=2, adsorbent to biomass=1.0 and catalyst to biomass=0.1 (all in mass ratio)

Fig. 3 shows SO<sub>2</sub> concentration profiles at 600, 675 and 750°C. SO<sub>2</sub> concentration varies in the range of 100-210 ppm in the temperature range of 600-675°C. However, SO<sub>2</sub> profiles first attained a value of about 200 ppm while later stabilized (after 36 min) at ~100 ppm for 600°C. Similarly, the concentration at 675°C reached to a value about to 200 ppm but stabilized at 350-400 ppm (after 36 minutes). Much higher concentration of 800-1000 ppm was observed at highest temperature of 750°C. The lowest concentration of SO<sub>2</sub> at lower temperature of 600-675°C as compare to high temperature of 750°C might be explained due to the high reactivity of CaO (bed material) at lower temperature (600-675°C). This high activity of CaO at temperature range of 600-675°C was verified by the authors in the previous study (Khan et al., 2014b). The application of CaO adsorbent to remove SO<sub>2</sub> in combustion and gasification plants was well supported by the literature (C. H. Nelli and Rochelle, 1998; Khan and Gibbs, 1996, 1997; Khan et al., 2012; S. V. Loo, 2002). Additionally, NO and SO<sub>2</sub> followed similar concentration profiles at 750°C and attained a high value of 1000 ppm.

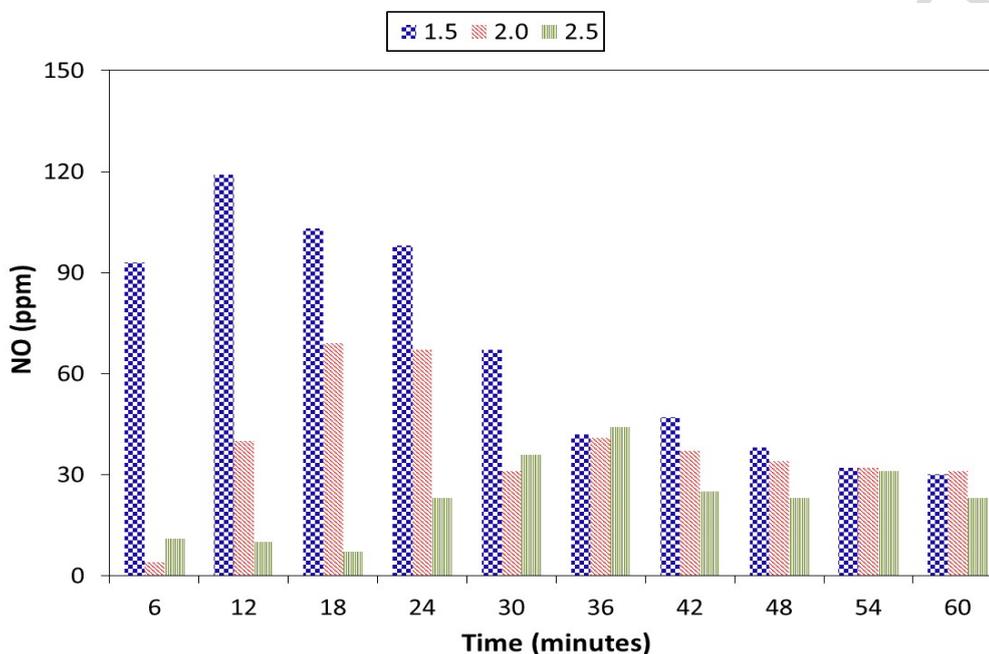


**Fig. 3.** SO<sub>2</sub> concentration with variable temperature at steam to biomass =2.0, adsorbent to biomass =2.0 and catalyst to biomass=0.1

### 3.2 Influence of steam to biomass ratio

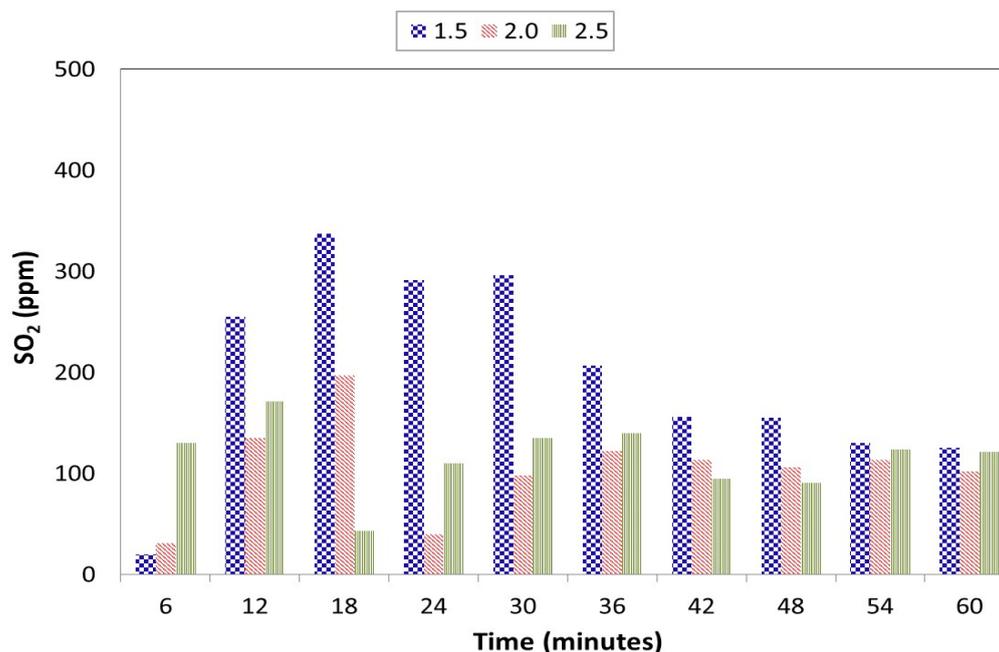
The concentration profiles of NO and SO<sub>2</sub> with variable steam to biomass ratio of 1.5, 2.0 and 2.5 are shown in Fig. 4 and 5. Fig. 4 shows the NO concentration profile in the product gas with variable steam to biomass ratio. At low steam to biomass of 1.5, high NO formation of 119 ppm was observed in first 12 minutes which was continuously decreased and stabilized at its lowest value of 30 ppm. Similar trends were observed for steam to biomass ratio of 2.0 but initial concentration was about 60 ppm at first 12 minutes. However, NO concentration profiles at steam to biomass of 2.5 was slightly different and initiated at lowest value of 10 ppm but stabilized at <30 ppm which was the lowest among all three steam to biomass ratios. The amount of steam injected at different steam to biomass ratios may be a reason for lower NO concentration at high steam to biomass ratio. However, all steam to biomass ratios reached to similar values at 36-60 minutes which might be helpful to select an optimum amount of steam required for minimum NO concentration. Once the oxygen content is swept away by the steam in the gasifier, the amount of NO formation at constant biomass feed rate might be constant for different amount of steam. However, the initial NO concentration profiles observed were different at variable

steam to biomass ratios which may be inferred that the different amount of steam requires different time to sweep away any oxygen content produced in the process. The steam addition can do a cooling effect and reduce the NO concentration at certain level. This was also observed by other researchers as well (Patel, 2001).



**Fig. 4.** NO concentration with variable steam to biomass ratio at 675°C, adsorbent to biomass =1.0 and catalyst to biomass=0.1

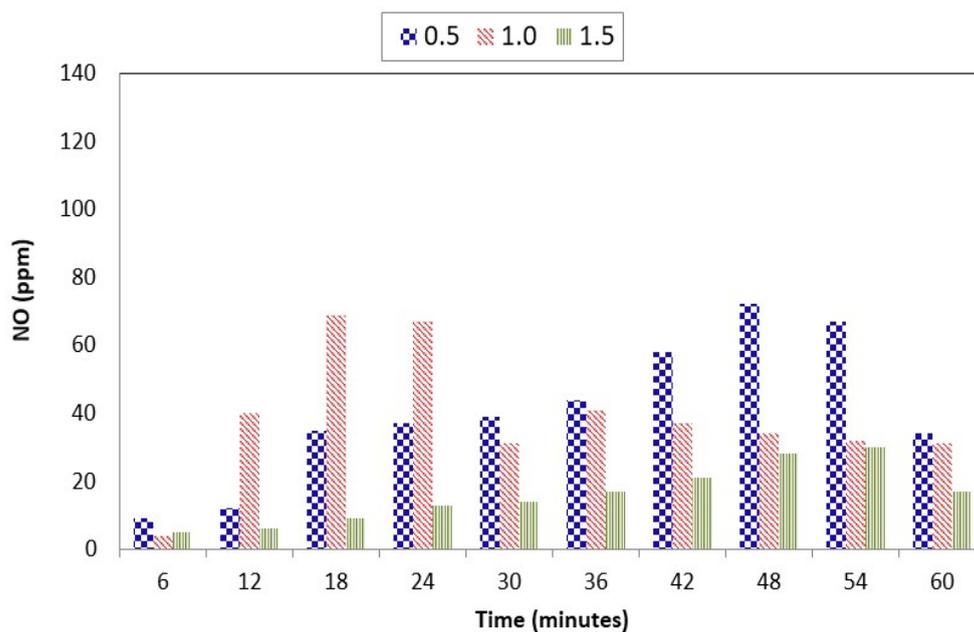
Fig. 5 shows the SO<sub>2</sub> concentration profiles with respect to different steam to biomass ratio of 1.5, 2.0 and 2.5. SO<sub>2</sub> profiles observed were like NO formation. Different initial concentration observed at steam to biomass ratio of 1.5, 2.0 and 2.5, the averaged concentration profiles were similar at reaction time of 36-60 minutes. The initial concentration profiles were found to be similar as observed in NO formation. Likewise, SO<sub>2</sub> generation profile found similar trends as NO formation by varying steam to biomass ratio. Likewise, the injected steam in the reactor took away any oxygen content generated in the process helps to produce O<sub>2</sub> deficient environment. The lower SO<sub>2</sub> concentration at high reaction time (> 42 minutes) of gasification process may be a justification to the argument.



**Fig. 5** - SO<sub>2</sub> concentration with variable steam to biomass ratio at 675°C, adsorbent to biomass =1.0 and catalyst to biomass=0.1

### 3.3 Effect of adsorbent to biomass ratio

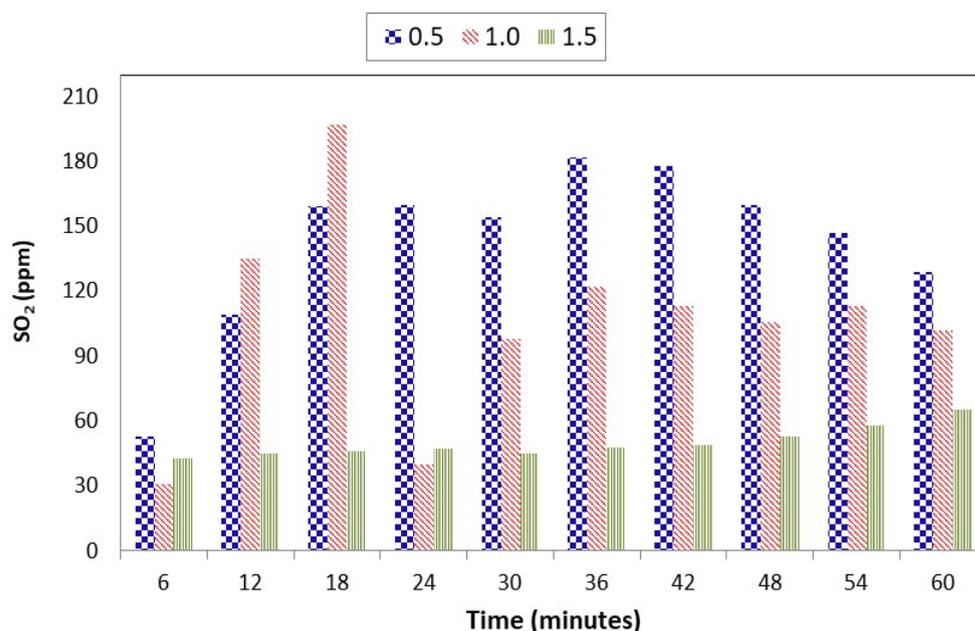
Fig. 6 provides the NO concentration profile with variable adsorbent to biomass ratio of 0.5, 1.0 and 1.5. At 0.50 of adsorbent to biomass ratio, the NO formation was stabilized at 40 ppm for first 36 min of gasification and continuously approached to a maximum value of 72 ppm followed by a sudden drop to 34 ppm. For adsorbent to biomass ratio of 1.0, NO generation reached to highest value of 67 ppm at 24 min after which it acquired steady state value of 32 ppm. Here, the comparison can be made based on the steady state values at 0.5 and 1.0. The comparison showed that the steady state values of NO at 1.0 (~ 40 ppm) was lower than at 0.5 (~32). At adsorbent to biomass ratio of 1.5, NO attained the lowest values of <30 ppm which was lowest amongst all three adsorbent to biomass ratios. The order of NO generation from maximum to minimum based on the adsorbent to biomass ratio was 0.5 > 1.0 > 1.5.



**Fig. 6.** NO concentration with variable adsorbent to biomass ratio at 675°C, steam to biomass =2.0 and catalyst to biomass=1.0

Fig. 6 demonstrates the effect of adsorbent to biomass ratio on composition of  $\text{SO}_2$  in product gas. The profiles were similar to NO formation.  $\text{SO}_2$  concentration showed a decreasing trend with ratio was increased from 0.5 to 1.5. The maximum  $\text{SO}_2$  generation was approached to 178 ppm and then reduced to 129 ppm at the end. Meanwhile, at adsorbent to biomass ratio of 1.0, the values generated were first increased to 197 ppm followed by almost steady values of 110 ppm. At high adsorbent to biomass ratio of 1.5, the  $\text{SO}_2$  formation showed the value of ~ 50 ppm, which is the lowest amongst all the three adsorbent to biomass ratios. As adsorbent to biomass ratio increases,  $\text{SO}_2$  concentration significantly reduces in the product gas.

In this study, the effect of variable adsorbent to biomass ratio has shown a potential effect on the  $\text{SO}_2$  and NO content in the product gas. This is due to the fact that CaO based compound was being used as adsorbent to remove  $\text{NO}_x$  and  $\text{SO}_x$  in gasification of coal, biomass burning and co-firing processes (C. H. Nelli and Rochelle, 1998; S. V. Loo, 2002). However, the complete data profiles from these power generation plants are rarely available and cannot be found in the open literature.

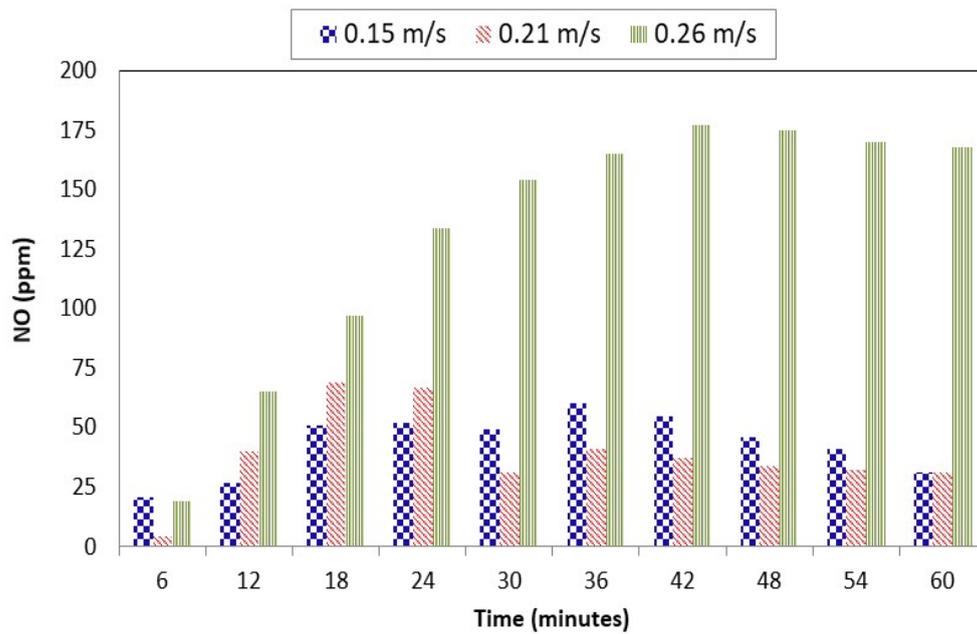


**Fig. 7.** SO<sub>2</sub> concentration with variable adsorbent to biomass ratio at 675°C, steam to biomass =2.0 and catalyst to biomass=0.1

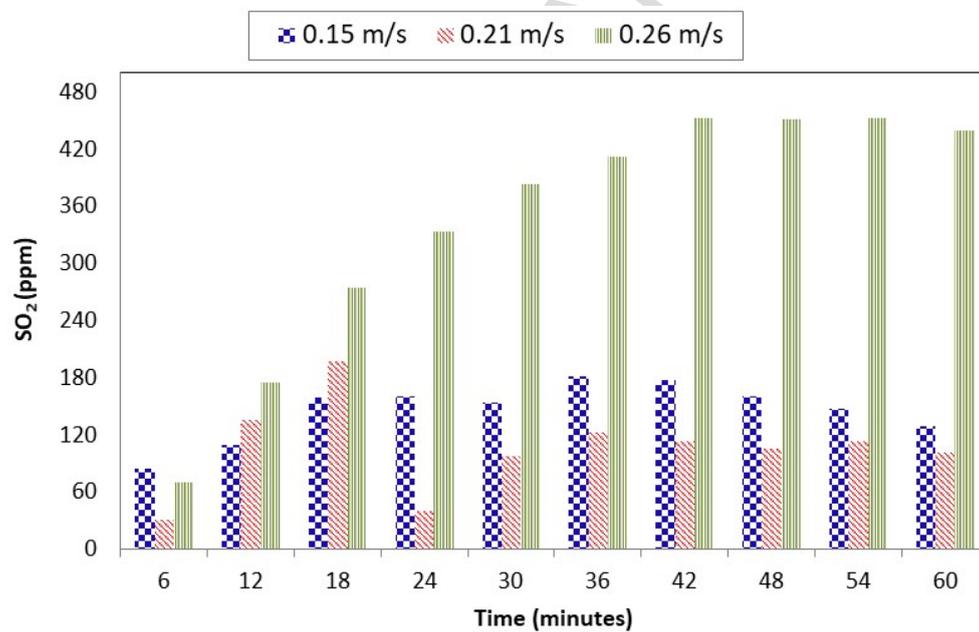
### 3.4 Effect of superficial velocity

The effect of superficial velocity on SO<sub>2</sub> and NO emissions is shown in Fig. 8 and 9. The investigations were conducted at three different fluidization velocities i.e. 0.15, 0.21 and 0.26 m/s at temperature of 675°C, steam to biomass ratio of 2.0, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1.

Fig. 8 shows the NO formation at different superficial velocities. The biomass flow rates were 1.0, 1.35 and 1.700 kg/h at 0.15, 0.21 and 0.26 m/s, respectively. The values were at their maximum for 0.15 and 0.21 m/s at first 24 min and then gradually reduced to a lowest value of 31 ppm. For 0.26 m/s, NO generation showed highest concentration of 170 ppm which is the maximum amongst all the superficial velocities. High values for NO formation was due to the high biomass feed rate of 1.70 kg/h associated with high superficial velocity (Khan et al., 2018b). SO<sub>2</sub> formation followed similar trend (Fig. 9). The steady values of SO<sub>2</sub> generated were 180, 110 and 450 ppm at 0.15, 0.21 and 0.26 m/s, respectively. Likewise, very high SO<sub>2</sub> concentration was due to the high biomass flow rate associated with high velocity of 0.26 m/s.



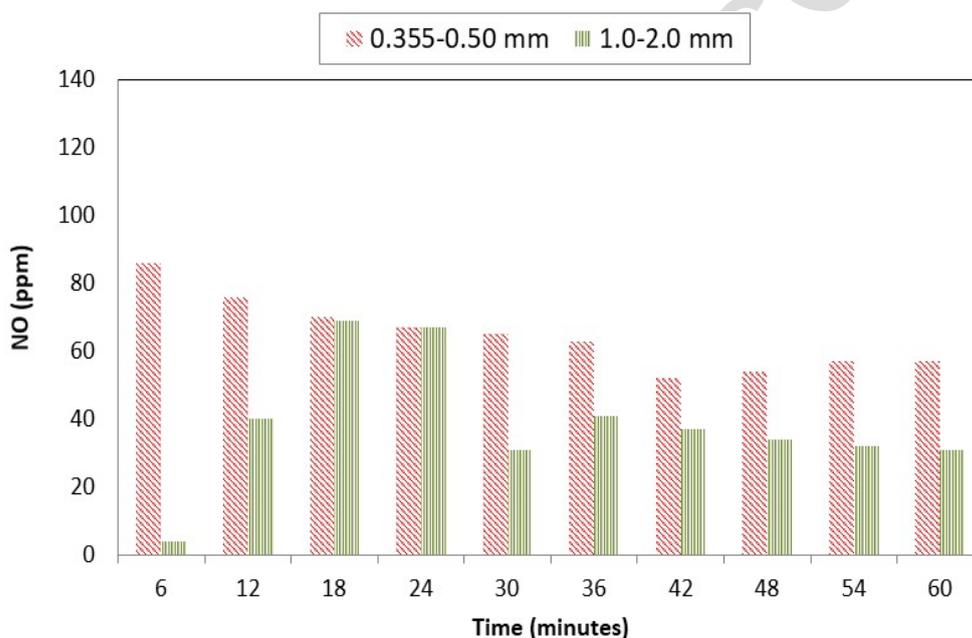
**Fig. 8.** NO concentration with variable superficial velocity at 675°C, adsorbent to biomass =1.0, steam to biomass =2.0 and catalyst to biomass=0.1



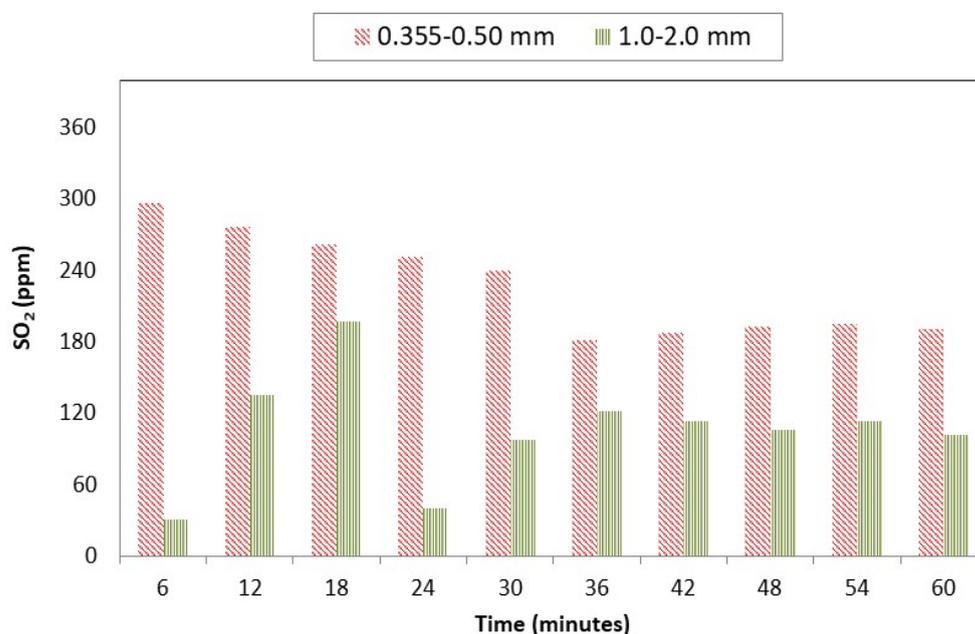
**Fig. 9.** SO<sub>2</sub> concentration with variable superficial velocity at 675°C, adsorbent to biomass =1.0, steam to biomass =2.0 and catalyst to biomass=0.1

### 3.5 Effect of biomass particle size

Fig. 10 shows NO formation with different biomass particle sizes of 0.355-0.50 and 1.0-2.0 mm at biomass flow rate of 1.35 kg/h. For small particle size, NO formation was in a range of 67-86 ppm which was then decreased and acquired steady values at 57 ppm. For larger particle, NO generation first observed to its maximum value and the decreased followed by steady state at 31 ppm. As observed, lower particle generated high NO in product gas than that of large particle. This may be due to the high capability of small particles to decompose where elemental N further react with limited oxygen content to produce NO.



**Fig. 10** - NO concentration with variable biomass particle size at superficial velocity of 0.21 m/s, at 675°C, adsorbent to biomass =1.0, steam to biomass =2.0 and catalyst to biomass=0.1



**Fig. 11** SO<sub>2</sub> concentration with variable biomass particle size at superficial velocity of 0.21 m/s, at 675°C, adsorbent to biomass =1.0, steam to biomass =2.0 and catalyst to biomass=0.1

Fig. 11 illustrates the SO<sub>2</sub> formation with variable biomass particle size. The trends were almost similar as observed in NO formation. The steady values of SO<sub>2</sub> produced were around 190 ppm and 110 ppm at 0.355-0.50 and 1.0-2.0 mm, respectively. Likewise, small biomass particle produces high SO<sub>2</sub> content in the product gas as compared to large particle.

In conclusion, lower temperature of gasification, higher steam to biomass ratio, higher ratio of adsorbent to biomass and large biomass particles favors low SO<sub>2</sub> and NO emissions in PKS catalytic steam gasification integrated with *in-situ* CO<sub>2</sub> adsorbent. The present study provides an initial insight on NO and SO<sub>2</sub> generation during steam gasification of biomass which has not been reported yet.

### 3.6 Comparative evaluation with commercial plants

The present study for NO and SO<sub>2</sub> emissions are compared with the pilot, commercial plants and local Air Quality Standard (AQS, Malaysia). However, the complete data profiles at similar operating conditions from power generation plants are rarely available and cannot be found in the open literature. The minimum average NO and SO<sub>2</sub> concentration of 16 ppm and 46 ppm, respectively, was observed at 675°C, steam to biomass ratio of 2.0 (wt/wt), adsorbent to biomass ratio of 1.5 (wt/wt) and catalyst to

biomass ratio of 0.1 (wt/wt). For pilot plants, Sethuraman et al. (2010) studied wood as a feedstock in fluidized bed reactor via air gasification at temperature of 815°C and found 215 ppm of NO concentration. Besides, the present study was further compared with the commercial gasification plants. The indirect heated fluidized bed gasification system by Manufacturing and Technological Conversion International (MTCI) observed almost similar concentration of NO (25 ppm) utilizing pulp sludge which might be due to similar oxidation agent (steam)(J.P. Ciferno and Marano, 2002). Studies reported by Patel et al. (Patel, 2001) was operated at high temperature (>840°C) and thus produced high NO concentration. Similar observations were also reported for SO<sub>2</sub> formation.

The NO and SO<sub>2</sub> generation in the present study was further compared with local Air Quality Standards (AQS) of Malaysia. The air quality standards permit NO and SO<sub>2</sub> concentration of 0.17 ppm and 0.13 ppm, respectively, based on averaging time of 1.0 hour (Asian Development Bank, 2006). This shows a huge challenge ahead for the future biomass power plants especially when using air as an oxidizing agent. This further emphasis on the use of NO and SO<sub>2</sub> reduction technologies integrated with biomass and co-gasification in commercial plants.

#### 4. Conclusions

The study provides an insight of NO and SO<sub>2</sub> emission from palm kernel shell steam gasification integrated with CO<sub>2</sub> adsorption and Ni catalyst in pilot scale fluidized bed system for cleaner production of hydrogen. Temperature with other four unique process variables i.e. steam to biomass ratio, adsorbent to biomass ratio, catalyst to biomass ratio, fluidizing gas velocity and biomass particle size in steam gasification using palm kernel shell are investigated which is not reported in the literature. Some key findings are summarized as follow.

- The temperature found to be the most influential variable whereas high steam to biomass ratios (2.5 wt/wt) significantly reduce NO (<30 ppm) and SO<sub>2</sub> (<110 ppm) formation in product gas to produce clean hydrogen.
- Consequently, similar trends were also observed for adsorbent to biomass ratio of 0.5-1.5 (wt/wt).

- Besides, fluidization velocities were found proportional to emissions where small particle size contributed to high concentration of NO and SO<sub>2</sub>.
- The average minimum NO (16 ppm) and SO<sub>2</sub> (46 ppm) concentration was observed at 675°C, steam to biomass ratio of 1.5, adsorbent to biomass ratio of 2.5 and catalyst to biomass ratio of 0.1.
- The results were found satisfactorily while comparing with commercial biomass power plants utilizing wood, municipal solid waste and pulp sludge for cleaner production of hydrogen.

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## Highlights

- NO and SO<sub>2</sub> emissions from catalytic steam gasification with in-bed CO<sub>2</sub> adsorption.
- Temperature is found to be the most influential, and proportional variable.
- Minimum concentrations of NO (30 ppm) and SO<sub>2</sub> (110 ppm) are observed at 600°C.
- High steam and adsorbent to biomass ratios (2.5 and 1.5 wt/wt) reduce NO and SO<sub>2</sub>.
- Large fluidization velocity and biomass size enhance NO and SO<sub>2</sub> emissions.