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# Experimental Study on Pyrolysis/Gasification of Biomass and Plastics for H<sub>2</sub> Production under New Dual-support Catalyst

Yue Chai<sup>a,b</sup>, Meihong Wang<sup>b,\*</sup>, Ningbo Gao<sup>a,\*</sup>, Yihang Duan<sup>a</sup>, Jiaqi Li<sup>a</sup>,

*a. School of Energy and Power Engineering, Xi'an Jiaotong University, 28 Xianning West Road, Xi'an, China.*

*b. Department of Chemical and Biological Engineering, The University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK.*

\*Corresponding authors:

E-mail addresses: [Meihong.Wang@sheffield.ac.uk](mailto:Meihong.Wang@sheffield.ac.uk) (M. Wang); [nbogao@xjtu.edu.cn](mailto:nbogao@xjtu.edu.cn) (N. Gao)

## Abstract

Energy security and environmental pollution are two major concerns worldwide. H<sub>2</sub> from pyrolysis/gasification of biomass and waste plastics is a clean energy source. However, relatively low yield and composition of H<sub>2</sub> is produced using this technology, thus preventing its commercialisation. Catalyst is key to promote H<sub>2</sub> production. This paper aims to explore whether newly developed dual-support catalyst Ni-CaO-C can catalyse gasification of volatiles from pyrolysis of different plastics (e.g. high density polyethylene - HDPE, polypropylene - PP and polystyrene - PS) and biomass (e.g. pine sawdust) for H<sub>2</sub> production. Experiments with and without catalysts were performed to test the performance of catalyst Ni-CaO-C. Impact of changing operating conditions (i.e. feedstock ratio, reforming temperature and water injection flowrate) on H<sub>2</sub> production were also investigated. Results show that catalysts (Ni-Al<sub>2</sub>O<sub>3</sub> or Ni-CaO-C) can effectively promote H<sub>2</sub> production. The H<sub>2</sub> production using catalyst Ni-CaO-C is much better than catalyst Ni-Al<sub>2</sub>O<sub>3</sub>. The catalytic effect of Ni-CaO-C rank in the sequence of HDPE > PP > PS. Plastic content in feedstock is suggested to be less than 40 wt% (for HDPE and PP) and 30 wt% (for PS) when mixing with biomass to reach high H<sub>2</sub> production. When the feedstock ratio is constant, high H<sub>2</sub> yield (i.e. 80.36 mmol/g) is achieved under relatively

low reforming temperature at 700 °C and water injection flowrate at 5 mL/h. However, under the same conditions, PP and PS only have H<sub>2</sub> yields at 59.35 mmol/g and 38.51 mmol/g. PS requires even higher temperature (800°C) and water injection flowrate (10 mL/h) to ensure acceptable H<sub>2</sub> yields. The new findings presented in this paper can help large scale commercial application of pyrolysis/gasification technologies for biomass and waste plastics.

Key words: Pyrolysis; Gasification; Biomass; Plastics; Catalyst; H<sub>2</sub> production

## **1. Introduction**

### **1.1 Background**

With centuries of development of human civilisation, two important problems of energy security and environmental pollution emerge as serious concerns (Jacobson, 2008). Energy security is caused by excessive depletion of traditional fossil fuels. Renewable energy is necessary to solve the potential energy supply shortage problems in future. Environmental pollution becomes more severe after consuming fossil fuels for electricity generation, industrial manufacturing and other activities. Gas emissions such as CO<sub>2</sub> are released into atmosphere to result in global warming and climate change. Solid wastes such as plastics are produced and then discarded considerably every year, which are harmful to creatures in land and aquatic environment (Law, 2017). Therefore, a kind of new renewable energy resource with low burden on environment is required urgently. To solve these two problems at the same time, technology of pyrolysis/gasification of biomass and plastics for H<sub>2</sub> production is put forward.

Biomass is a good raw material for energy supply with renewable characteristics and low negative influence on environment because a carbon-neutral process can be realised when biomass is used to provide energy (Mazumder and Lasa, 2016). As one of the mostly used synthesised material, plastics is generated in large amount annually and it should take centuries to naturally decompose plastics (Verma et al., 2016). In 2017, around 348 million tonnes of plastics were produced (PlasticsEurope, 2018) and nearly 55 % of plastics were discarded

(Geyer et al., 2017). Plastics has a wide range of categories. Normally used plastics include high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS). Diversities exist in the physical and chemical properties of different plastics due to different microstructure.

H<sub>2</sub> is one of the main gas products from pyrolysis/gasification. However, there are problems influencing H<sub>2</sub> production effectively when only biomass or plastics is used for pyrolysis/gasification. Biomass is rich in oxygen content, which can result in high yields of char and tar (Alvarez et.al., 2014). Plastics is easy to be soften and stuck on the surface of reactor tubes, which restricts smooth feeding of feedstocks (Block et al.,2018). Therefore, combination of biomass and plastics as feedstock for pyrolysis/gasification is put forward to improve H<sub>2</sub> production.

## **1.2 Current progress in pyrolysis and gasification of biomass and plastics**

Previous studies investigated the advantages of pyrolysis/gasification of biomass and plastics (Alvarez et al., 2014; Zhang et al., 2016; Block et al.,2018; Burra et al., 2018; Esfahani et al., 2017 and CaO et al., 2020). They include: (i) the feedstock of this technology has stable source because biomass is renewable and plastics is discarded in large quantity; (ii) plastics can be decomposed through pyrolysis/gasification totally within minutes or hours, avoiding long term and low efficient treatment method such as landfill; (iii) H<sub>2</sub> can be obtained as product for energy supply; (iv) biomass is carbon neutral and H<sub>2</sub> is clean energy, less damage will be imposed to environment; (v) H<sub>2</sub> production can be promoted due to synergic effect of biomass and plastics compared to when only biomass or plastics is used for pyrolysis/gasification. However, this kind of improvement on H<sub>2</sub> production is still limited. There is still a long way for large scale commercialisation of this technology. Therefore, innovation is still strongly required to promote H<sub>2</sub> production in pyrolysis/gasification of biomass and plastics.

As researches continue to develop, one of the research hot topics in pyrolysis/gasification of biomass and plastics is to develop new catalyst with high catalytic activity to improve the H<sub>2</sub>

production. Nickel is one of the commonly used active core attached on different catalyst supports, accelerating the gasification reactions. Among various catalyst supports, CaO and activated carbon are good choices due to their unique properties. CaO is an excellent CO<sub>2</sub> adsorbent, which is used to improve the H<sub>2</sub> composition through reducing CO<sub>2</sub> composition in gaseous products. Activated carbon can effectively increase total gas yields (including H<sub>2</sub> yield) due to its special physical and chemical properties. There are many previous studies focusing on using CaO or activated carbon as catalyst support (see Table 1). For newly developed catalyst, it is important to test the performance of new catalyst when catalysing different combinations of biomass and plastics.

**Table 1 Previous studies using CaO or activated carbon as catalyst/catalyst support**

Publications	Catalyst	Feedstock(s)	Agent	Equipment	Application
Hu and Huang (2009)	CaO	Wet biomass (Pine sawdust)	Steam	One-stage fixed bed reactor	Hydrogen production
Acharya et al. (2010)	CaO	Biomass (Pine sawdust)	Steam	One-stage fixed bed reactor (Stainless steel cylinder tube)	Hydrogen production
Wu and Williams (2010a)	Ni-Mg-Al-CaO	Plastic (polypropylene)	Steam	Two-stage fixed bed reactor	Hydrogen production
Kumagai et al. (2015)	Ni-Mg-Al-Ca	Biomass and plastic (Wood sawdust and polypropylene)	Steam	Two-stage fixed bed reactor	Hydrogen production
Sun et al. (2017)	CaO-HZSM-5	Biomass (Wood sawdust)	Air	One-stage fixed bed reactor	Hydrogen and bio-oil production
Liu et al. (2018)	Fe <sub>2</sub> O <sub>3</sub> , CaO	Microalgae	Air	One-stage fixed bed reactor	Hydrogen production

Publications	Catalyst	Feedstock(s)	Agent	Equipment	Application
Nanou et al., (2013)	Char	Biomass ( Pine wood)	Steam	Thermogravimetric analyser	Reactivity analysis
Cho et al. (2015)	Ni-C, Fe <sub>2</sub> O <sub>3</sub> , MgO, Al <sub>2</sub> O <sub>3</sub>	Plastic (PVC)	Air	One-stage fluidised bed reactor	Hydrogen production
Yao et al. (2016)	Ni-C	Biomass (Wheat straw)	Steam	Two-stage fixed bed reactor	Hydrogen production
Ren et al. (2017)	Ni-C	Biomass volatiles (from corn hub pyrolysis )	Steam	Two-stage fixed bed reactor	Hydrogen production
Ravenni et al. (2019)	Char or activated carbon	Tar model compounds (toluene-naphthalene)	Steam	One-stage fixed bed reactor	Tar removal

### 1.3 Motivations for this study

The main driver for our series of study is to improve the H<sub>2</sub> production from co-pyrolysis/gasification of biomass and plastics under the newly developed catalyst. As an ideal energy source, H<sub>2</sub> has several advantages compared to fossil fuels: (i) H<sub>2</sub> is rich in energy content with lower heating value (LHV) 120 KJ/g, which is nearly three times as that of gasoline (Møller et al., 2017); (ii) H<sub>2</sub> could be generated from electrolysis, gasification or other methods from renewable sources such as biomass; (iii) H<sub>2</sub> is totally clean because only water is produced after H<sub>2</sub> combustion; (iv) H<sub>2</sub> can be used in many ways in addition to direct combustion (Kumar et al., 2009). H<sub>2</sub> can also be used in fuel cell for electricity generation or be used in Fisher-Tropsch synthesis process for liquid fuels production. In summary, H<sub>2</sub> is a promising new energy which deserves more attention. Thus new technology for high H<sub>2</sub> production should be investigated.

The motivation of this study is to test the performance of new catalyst Ni-CaO-C when catalysing co-pyrolysis/gasification of biomass and different plastics. Catalyst is key to

improve the H<sub>2</sub> production (Kwon et al., 2018; Saleem et al., 2020). However, waste plastics is complicated in compositions. Catalytic effect may diverse for different plastics due to different physical and chemical properties. Cost will increase if waste plastic is separated into specific categories for thermo-chemical treatment. Therefore, it is necessary to test whether new catalyst is available to keep high catalytic activity when encountering different combinations of plastics and biomass. In addition, the influences of operating conditions on H<sub>2</sub> production using new catalyst are also important to be investigated.

#### **1.4 Aim of this study**

In our previous study (Chai et al., 2020), a new dual-support catalyst Ni-CaO-C was synthesised. The main aim was to test the feasibility and performance of the new Ni-CaO-C catalyst and only one kind of plastics (LDPE) was mixed with biomass for pyrolysis/gasification. More importantly, it was necessary to select the best Ni loads and support ratio of CaO:C with the highest H<sub>2</sub> yield and composition. Therefore, series of experiments were carried out changing Ni loads (i.e. 0 wt%, 5 wt%, 10wt%, 15 wt% and 20wt%) support ratios (i.e. CaO:C= 0:10, 3:7, 5:5, 7:3 and 10:0). Eventually, the catalyst Ni-CaO-C with Ni load 10 wt% and CaO:C ratio 5:5 was selected due to the best performance with the highest H<sub>2</sub> yield and composition.

In this study, the aim is to test whether the new catalyst Ni-CaO-C is suitable to catalyse pyrolysis/gasification of different combinations of plastics (HDPE, PP and PS) and biomass (pine sawdust) for H<sub>2</sub> production. Series of experiments were performed to compare situations without and with catalysts. We also carried out TG-FTIR analysis for three different plastics to compare differences of plastics decomposition, which can give better understanding of performance of catalytic cracking and reforming from micro level. In addition, the influences of operating conditions (feedstock ratio, reforming temperature and water injection flowrate)

on H<sub>2</sub> production were also investigated when new catalyst Ni-CaO-C is used for different plastics mixing with biomass.

### **1.5 Novel contribution of this study**

In *section 1.2*, benefits using CaO or activated carbon as catalyst supports have been introduced. CaO is beneficial to promote H<sub>2</sub> composition. Activated carbon is helpful to promote total gas yield. However, drawbacks still exist for these two supports. CaO is weak to improve the H<sub>2</sub> yield because decreasing CO<sub>2</sub> composition can only influence water-gas-shift (WGS) reaction to change H<sub>2</sub> yield. When using activated carbon only, the H<sub>2</sub> composition in product gases is relatively low because the increasing yields of other gases simultaneously decrease H<sub>2</sub> composition. Therefore, a new idea is put forward to combine these two supports together to make the most use of their advantages and overcome their disadvantages to ensure high H<sub>2</sub> composition and yield at the same time. The new catalyst Ni-CaO-C combines CaO and activated carbon together as catalyst support to support active core Ni. Results indicate that the synergic effect of different components in catalyst Ni-CaO-C can achieve high H<sub>2</sub> production (i.e. with high H<sub>2</sub> yield and composition) simultaneously, which is also the main novelty of our previous study (Chai et al., 2020). However, only one kind of plastics (LDPE) was used to mix with biomass to test the performance of new catalyst Ni-CaO-C in that study. Therefore, the novelties of this study are summarised below:

(a) The H<sub>2</sub> production performance using different plastics with biomass under different situations were compared and summarised systemically.

As mentioned before, waste plastics is complicated in compositions, which is generally mixture of many different types of plastics. In this study, three pure plastics (i.e. HDPE, PP and PS) were mixed with biomass (pine sawdust) for experiments to examine the H<sub>2</sub> yield and composition under following situations: (i) only pyrolysis without catalyst; (ii) pyrolysis/gasification without catalyst; (iii) pyrolysis/gasification under traditional catalyst Ni-

Al<sub>2</sub>O<sub>3</sub>; (iv) pyrolysis/gasification under new catalyst Ni-CaO-C. The advanced properties of new catalyst Ni-CaO-C can be exhibited clearly when comparing to other situations and the catalytic performance of new catalyst Ni-CaO-C on three plastics (with biomass) are also ranked.

(b) H<sub>2</sub> yield performance was tested when feedstock ratio was changed. Experimental results show that excess higher plastics content in feedstock mixture cannot help to promote the H<sub>2</sub> yield.

In addition to comparing H<sub>2</sub> production with or without different catalysts, operating conditions such as feedstock ratio, reforming temperature and water injection flowrate were also changed to test influences on H<sub>2</sub> yield and composition under catalyst Ni-CaO-C when different combinations of plastics and biomass were used.

To summarise, the new findings in this paper can help large scale commercial application of pyrolysis/gasification technology. The attempt of using pure plastics under catalyst Ni-CaO-C can accumulate research experience for future attempt to use real plastic waste.

## **2. Materials and methods**

### **2.1 Materials**

Pine sawdust is used as biomass feedstock in this study and a 60 mesh filter was used to process the particle size. Table 2 shows proximate and ultimate analysis of biomass. The proximate analysis of pine sawdust was carried out in a muffle furnace (FO410C, Yamato, Japan) according to Chinese standard GB/T 212-2008, which is equivalent to American standard ASTM D 3172-89(2002). The ultimate analysis of pine sawdust was performed using an elemental analyser (EA 3000, Eurovector, Italy). Pure HDPE, PP and PS particles are used in experiments and the size of each particle is smaller than 5 mm. The reason why these three plastics were selected is that they are most widely used plastics over the world (Wu and Williams, 2010b). The plastic particles are provided by Shenhua Chemical Industry, China.

Only results of ultimate analysis of three plastics are shown in Table 3. According to Zhou et al. (2014), the volatiles composition of HDPE, PP and PS are all higher than 99 wt%. The specific chemical formula of plastics are also shown in Figure 1.

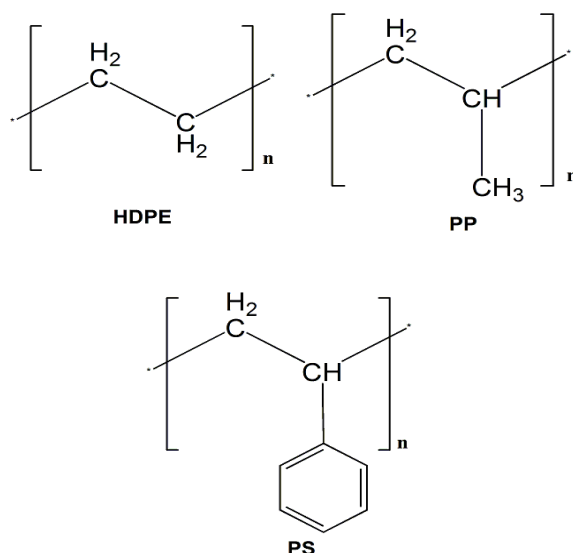
The other chemicals used in the experiments are shown below (Chai et al., 2019): Nickel in catalyst Ni-CaO-C derived from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Tianjin Yongshen Fine Chemical Ltd., China). Calcium acetate (Chengdu Kelong Chemical Ltd., China) was calcined under 850 °C using muffle furnace for 2 hours to produce CaO. Activated carbon was produced through petroleum coke activating by potassium hydroxide. 25 wt% ammonia solution (Tianjin Tianli Chemical Ltd., China) was used to control the pH during catalyst preparation.

**Table 2 Results of proximate and ultimate analysis of biomass (Pine sawdust)**

Proximate analysis		Ultimate analysis	
Moisture	2.77 wt%	C	49.17 wt%
Fixed carbon	13.91 wt%	H	6.36 wt%
Volatile matter	82.03 wt%	O	44.12 wt%
Ash	1.29 wt%	N	0.36 wt%

**Table 3 Results of ultimate analysis of plastics (HDPE, PP and PS)**

HDPE		PP		PS	
C	85.71 wt%	C	85.71 wt%	C	92.31 wt%
H	14.29 wt%	H	14.29 wt%	H	7.69 wt%
O	0 wt%	O	0 wt%	O	0 wt%
N	0 wt%	N	0 wt%	N	0 wt%



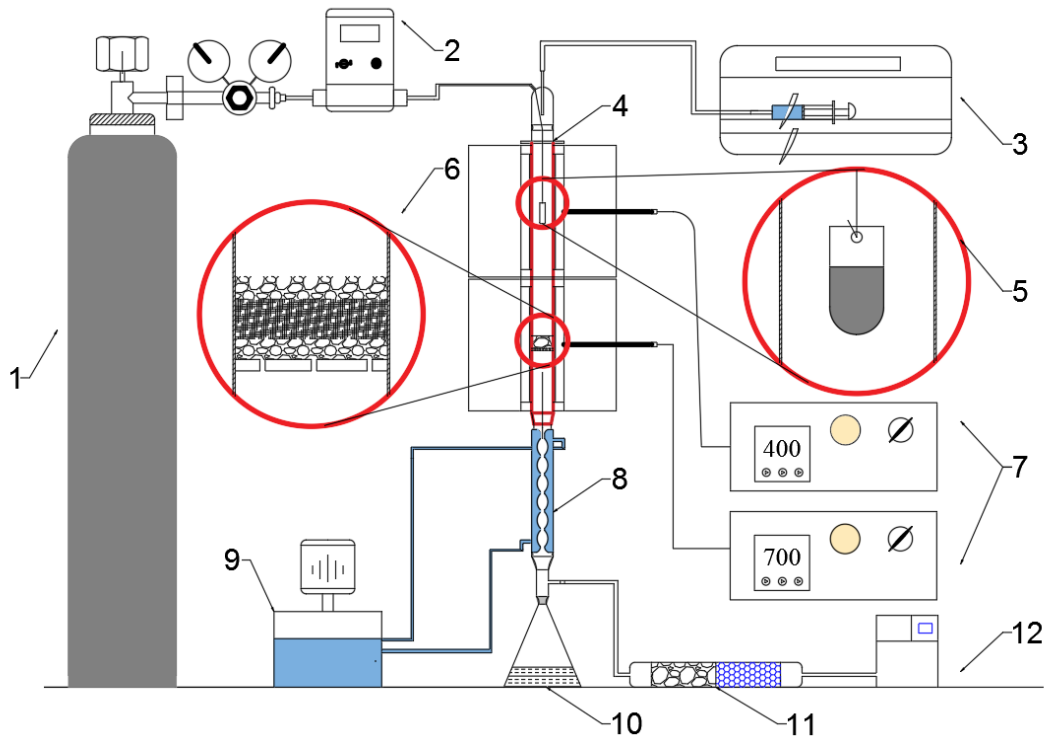
**Figure 1 Specific chemical formula of three plastics**

## 2.2 Catalyst preparation

In this study, new catalyst Ni-CaO-C was synthesised by rising pH method (Chai et al., 2020). (i)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in deionized  $\text{H}_2\text{O}$ . Then, 1 mol/L of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added into the solution until the pH of the solution reached 8.3 under 40 °C. This procedure was operated with moderate stirring. (ii) Heating and stirring were stopped when pH was 8.3. The solution was put aside for static settlement. After the solution was separated into two layers, the top transparent layer was removed and only the bottom green layer was left. Then, deionized water was added again until the total solution was 200 mL. (iii) CaO and activated carbon powder were added into the solution. The mixed solution was kept stirring for 12 h to ensure sufficient mixture. (iv) Eventually, the solution was put in oven at 105 °C until the water was totally evaporated. Then the dry catalyst precursor was calcined at 850 °C for 3 h under  $\text{N}_2$  atmosphere.

The specific catalyst used in this study is Ni-CaO-C with 10 wt% of Ni load. The rest 90 wt% of catalyst are consisted of two catalyst supports CaO and activated carbon. The support ratio (weight ratio) of two supports is 5:5 (i.e. CaO:C).

## 2.3 Experimental system



**Figure 2 Two-stage fixed bed pyrolysis/gasification system (Gao et al., 2018)**

(1. Nitrogen cylinder, 2. Mass flowmeter, 3. Microinjection pump, 4. Quartz reaction tube and heating furnaces, 5. Quartz crucible, 6. Catalytic layer: quartz wool + catalyst, 7. Temperature controllers, 8. Condenser pipe, 9. Cooling water and water pump, 10. Conical flask, 11. Dryer, 12. Gas chromatography)

A two-stage fixed bed reactor was used to carry out the pyrolysis/gasification experiment (Figure 2). For each stage of reactor, the height is 150 mm and the diameter is 30 mm. The feedstock mixture is put in the top stage and the catalyst is put in the bottom stage. Correspondingly, pyrolysis reactions occur in the top stage and reforming/cracking reactions occur in the bottom stage. Specific experimental procedures are summarised below (Chai et al., 2019):

(a) Quartz wool (i.e. *symbol 6* in Figure 2) was put in the bottom stage to support 0.5 g of catalyst (if catalyst was used in experiments). Mixture of biomass and plastics with total mass of 0.5 g was put in a quartz crucible (i.e. *symbol 5*) and fixed at the top stage.

(b) After checking the gas tightness of equipment, 60 mL/min of N<sub>2</sub> was kept blowing into

the reactor system for 20 mins to ensure oxygen-free (i.e. *symbol 2*).

(c) Then, the bottom stage was pre-heated to reach required reforming temperature (i.e. *symbol 7 bottom temperature controller*). After the bottom temperature was stable, the top stage began to be heated with heating rate of 30 °C /min (i.e. *symbol 7 upper temperature controller*).

(d) If water was required in experiments (i.e. gasification), water pump (i.e. *symbol 3*) started to inject water into system with certain flowrates (1 ml/h, 5ml/h or 10 ml/h) and the water was evaporated into steam instantly. The specific flowrate used for each experiment for is summarised in the following sections (Tables 4, 5 and 7).

(e) Then, switch on the cooling system (i.e. *symbol 9*) and connect gas collection bag with dryer (i.e. *symbol 11*) to collect gas products simultaneously.

(f) After 1 h reaction, gas collection was finished. The collected gas products were measured by a gas chromatography (GC) (GC7900, Tianmei Ltd., China) to detect the gas compositions and yields.

## **2.4 Characterisation of feedstocks and used catalysts**

Characterisation of plastic feedstocks (HDPE, PP and PS) could help to get in-depth understanding of the diversities of their properties, which is useful as proof to support further pyrolysis/gasification experimental studies. Thermogravimetric (TG) analysis coupled with Fourier Transform infrared spectroscopy (FTIR) analysis was applied to three plastics to identify the differences in thermal decomposition. Nearly 10 mg of plastics particles were heated in a TG analyser (DG-60, SHIMADZU, Japan) firstly and the operating conditions were controlled the same as that in the pyrolysis stage. The heating rate was 30 °C/min and the plastics were heated from room temperature to 800 °C under nitrogen atmosphere. During running of TG analysis, the decomposition products from TG analyser were directly transferred into a FTIR analyser (IR Affinity-1S, SHIMADZU, Japan) for analysis in real-time.

Characterisation of used catalysts through TG analysis will help to predict the coke formation extent after pyrolysis/gasification experiments. Nearly 10 mg of used catalyst was heated from room temperature to 800 °C (heating rate: 10 °C/min) under air atmosphere and the eventual temperature kept stable for 10 minutes before decreasing.

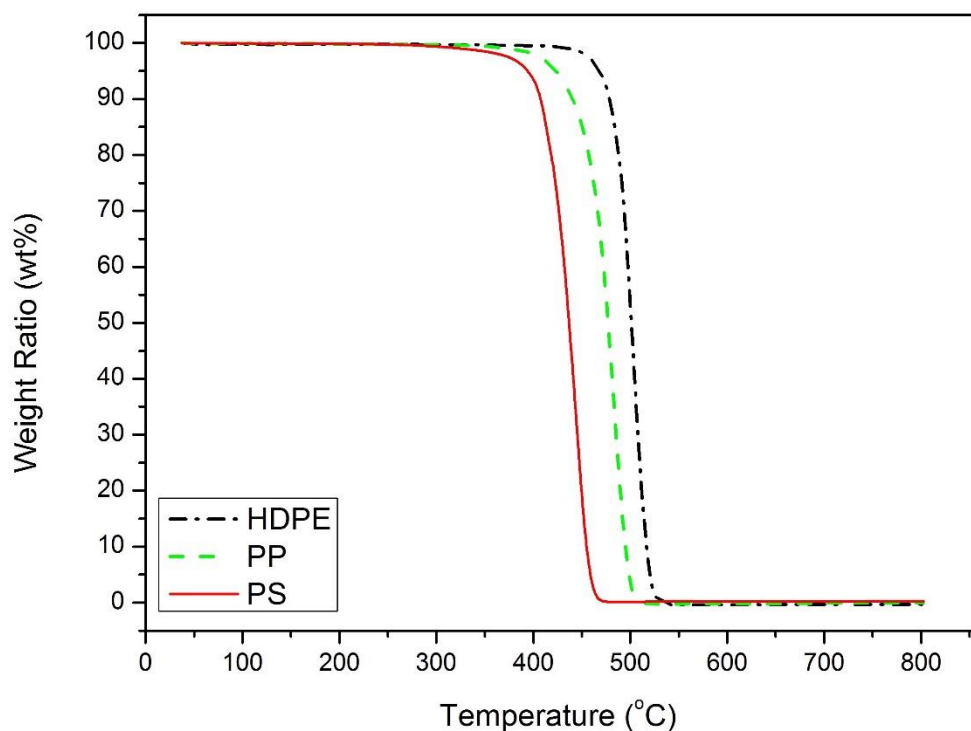
### **3. Results of feedstocks characterisation**

#### **3.1 TG analysis of the plastics**

TG analysis was performed under N<sub>2</sub> with the same heating rates (i.e. 30 °C/min) as that in the pyrolysis stage of two-stage fixed bed reactor (top stage in Figure 2). The results of TG analysis are shown in Figure 3.

From Figure 3, similar trends can be observed in curves for different plastics. Before 300 °C, the weight ratios of three plastics nearly keep constant. With temperature increasing, PS starts to lose weight obviously from 400 °C. PP and HDPE follow with obvious decreasing trend at 450 °C and 500 °C respectively. All the plastics end with weight ratios at around 0 wt%.

Majority of the plastic components are decomposed and released totally during pyrolysis. This also demonstrates that plastics is mainly consisted of volatiles and nearly no ash content is contained, which is consistent with the results of proximate analysis of plastics in *section 2.1*. Among three plastics, PS first completes weight loss process within the lowest temperature range (400 – 450 °C) and HDPE completes within the highest temperature range (500 – 550 °C) at last. However, only a lower decomposition temperature of feedstock cannot ensure a better eventual product yields of pyrolysis/gasification process. The specific composition of generated volatiles during pyrolysis also makes sense to influence extent of reactions in reforming stage. That is also the reason why FTIR analyser is connected with TG analyser to detect the composition of generated volatiles in real-time.



**Figure 3 Results of TG analysis of three plastics**

### 3.2 FTIR analysis of the plastics

The results of FTIR analysis are shown in Figure 4. The specific adsorption bands of FTIR spectrums are compared with published results from previous study (Jung et al., 2018) to identify the chemical groups. At 400 °C, peaks at around 2400  $\text{cm}^{-1}$  are observed for HDPE and PS, which are demonstrated to be  $\text{CO}_2$ . For PP, peak between 2800 – 3000  $\text{cm}^{-1}$  is observed, which is demonstrated to be C-H bending in alkane.

The experimental results for 400 °C can be explained: PP is rich in side chain methyl. Reactions during pyrolysis obey free radical principle, which is the same as the principle for thermal cracking (Moldoveanu, 2019). According to the free radical principle, methyl is the most active radical, requiring the lowest energy to be released. Even at low temperature, pyrolysis could help to break the bonds inside PP and released methyl is easy to produce alkane furthermore.

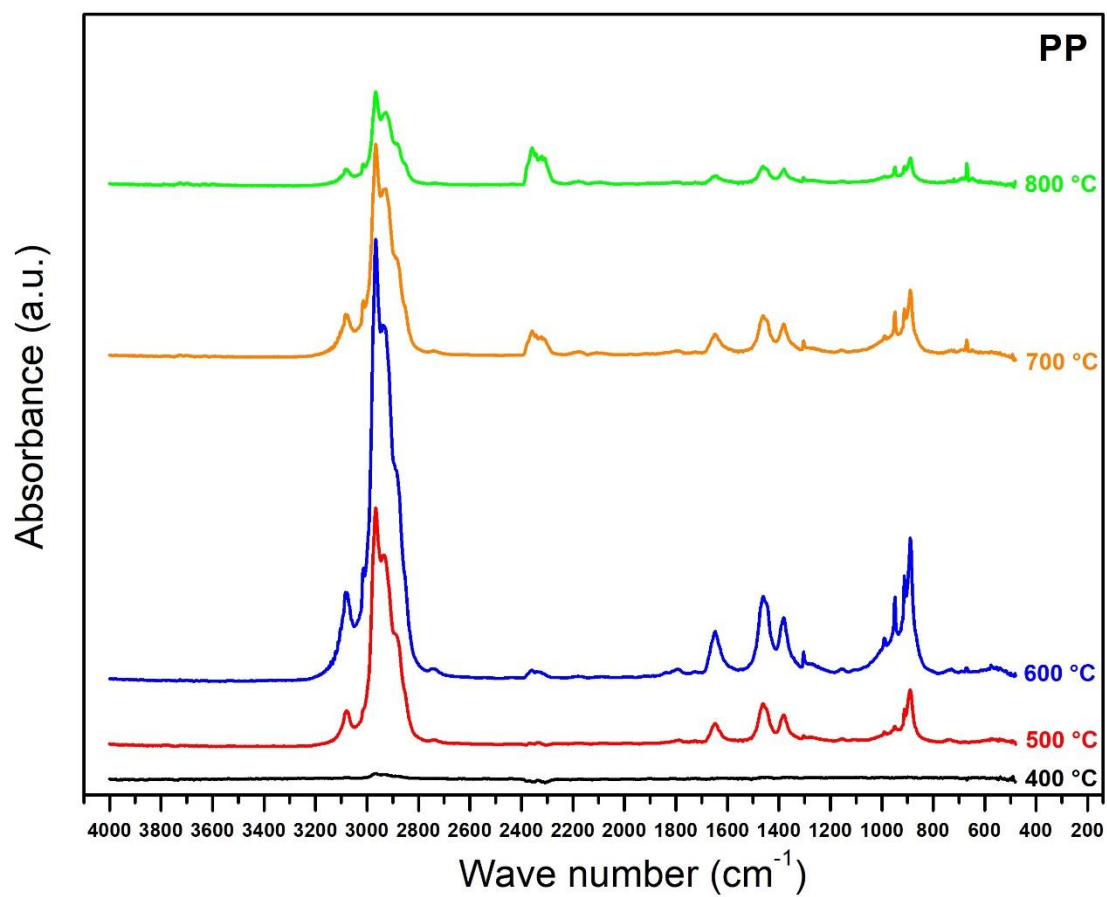
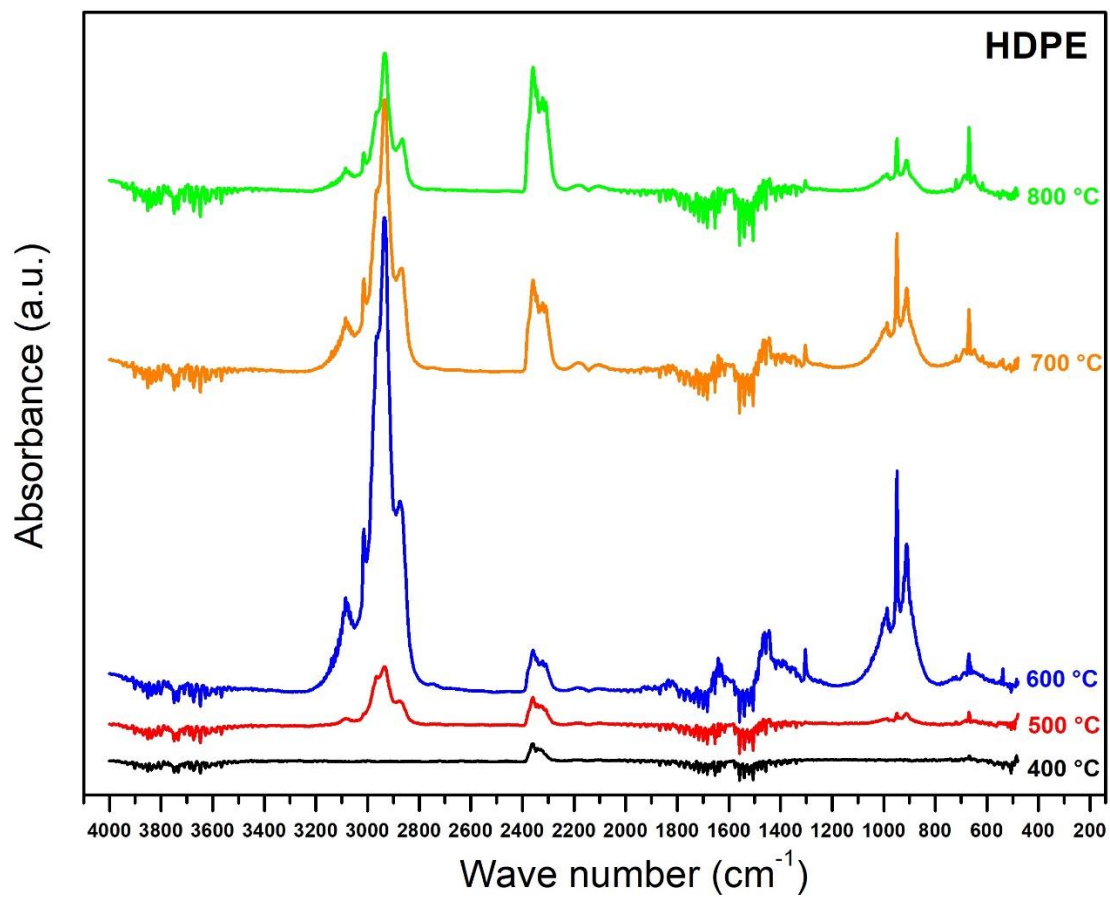
At 500 °C, for all the three plastics, peaks of  $\text{CO}_2$  (around 2400  $\text{cm}^{-1}$ ) with higher absorbance are observed compared to 400 °C. The peak of alkane (2800 – 3000  $\text{cm}^{-1}$ ) for HDPE and PP

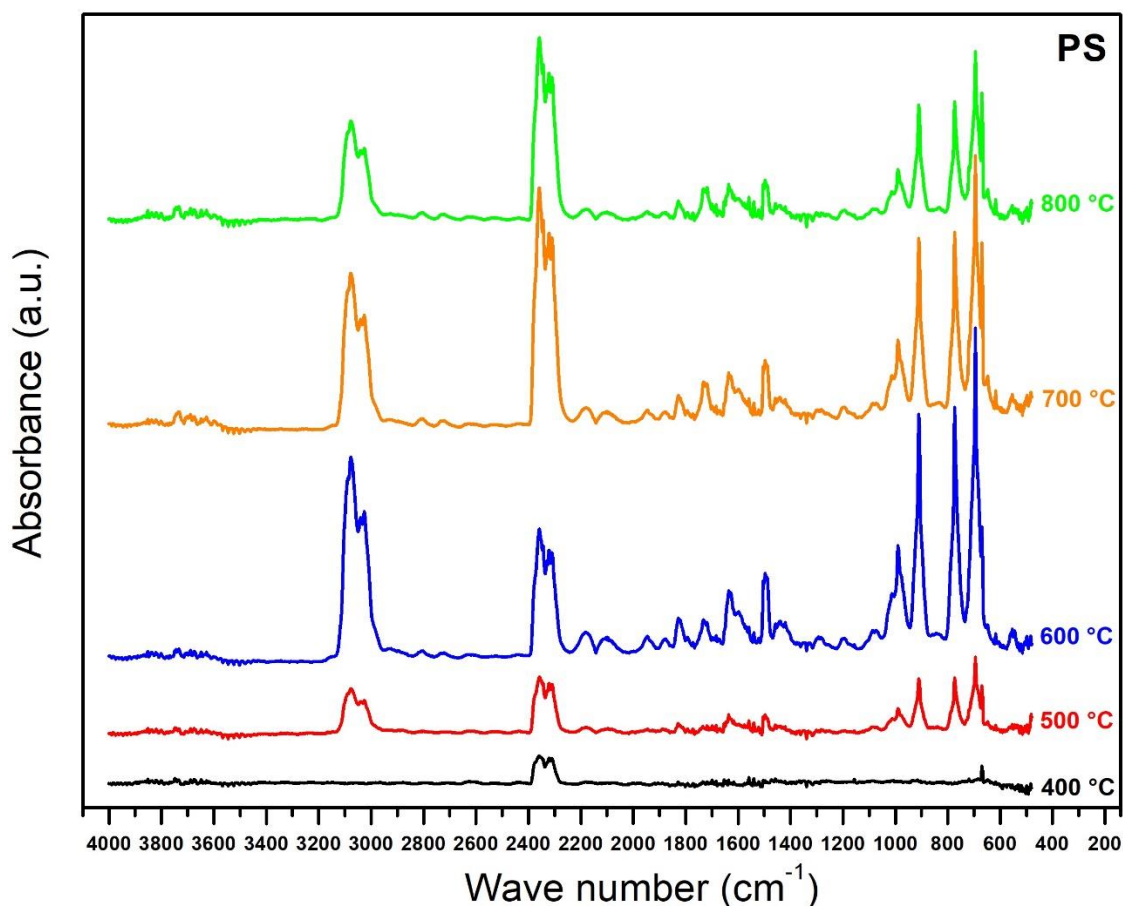
also become higher compared to 400 °C. Some new peaks are also observed. The peaks between 1300 – 1500 cm<sup>-1</sup> of PP are demonstrated to be C-H bending of methylene group and methyl group in generated alkane. For PS, peak at 700 ± 20 cm<sup>-1</sup> is benzene derivative and peak between 3000 – 3100 cm<sup>-1</sup> represents the C-H stretching in alkene.

The comparison between the cases for 400 °C and 500 °C can be explained as: According to Lambert-Beer law, the higher absorbance value at a specific adsorption band it has, the higher concentration of relevant generated product it represents (Gao et al., 2013). Therefore, the value of the absorbance generally reflects the quantity of generated chemicals. Compared to 400 °C, higher temperature (e.g. at 500 °C) promotes the extent of decomposition. This is reflected by increasing absorbance of existing products (i.e. CO<sub>2</sub> for three plastic and alkane for PP) and newly emerging products (i.e. alkane for HDPE and alkene for PP/PS).

At 600 °C, absorbance for existing peaks of three plastics becomes higher compared to 400 °C and 500 °C. New peak of alkene (3000 – 3100 cm<sup>-1</sup>) also appears for HDPE at 600 °C. For PS, new peaks of C-H bending in aromatics appear at 1650 – 2000 cm<sup>-1</sup>. When temperature further increases to 700 °C and 800 °C, the peaks of three plastics become lower. To summarise, several general findings are obtained from Figure 4:

(a) Alkane is the main product of HDPE pyrolysis. Pyrolysis helps to break the long chain structure of HDPE by decomposing heavier molecular weight compounds into lighter ones such as alkane and alkene. Alkane takes most proportion in products. Relative small amount of alkene is generated.





**Figure 4 Results of FTIR analysis of three plastics**

(b) Alkane and methyl are the main products of PP pyrolysis. C-H bending of methyl is very active to be broken according to free radical principle. On one hand, released free methyl combines with free H radical to form  $\text{CH}_4$ . On the other hand, it can form new saturated hydrocarbons through combining with other functional groups. This explains why PP has higher yield of alkane compared to HDPE. Alkene is also generated but in less quantity due to restriction of methyl.

(c) Alkene and benzene derivatives are main products of PS pyrolysis. The benzene in side chain of PS is rich in unsaturated bonds. Break of benzene requires higher energy compared to that of long chain structure of HDPE and PP. Considerable alkene is produced when C-H bending of benzene is broken during decomposition. Benzene derivatives are also detected as the aromatic is not decomposed timely.

#### 4. Experimental studies of pyrolysis and/or gasification of biomass and different plastics with/without catalyst

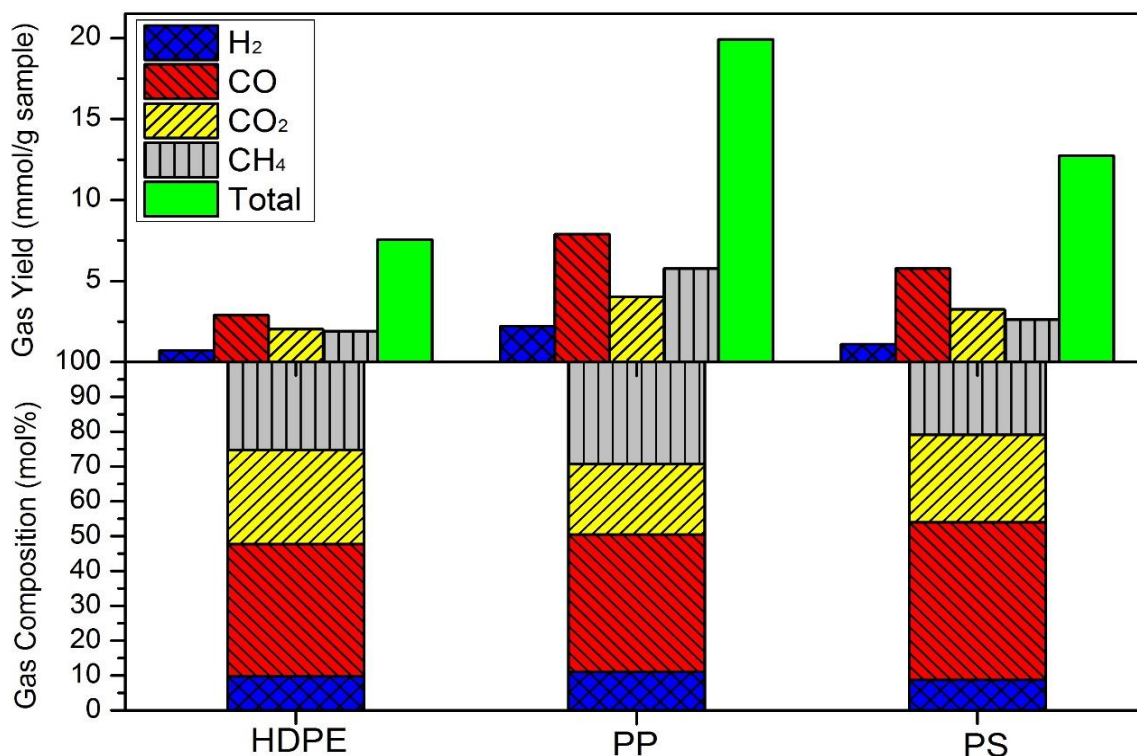
In this section, the catalytic activity and CO<sub>2</sub> adsorption capacity of the new catalyst Ni-CaO-C for biomass and different plastics are tested when compared to experiments without catalyst and experiments using traditional catalyst Ni-Al<sub>2</sub>O<sub>3</sub>.

##### 4.1 Pyrolysis/gasification of biomass and different plastics without catalyst

**Table 4** List of experiment studies for pyrolysis/gasification without catalyst

Exp.	Plastics	Feedstock ratio (Biomass: Plastics)	Pyrolysis T	Reforming T	Water injection
1	HDPE	5:5	800 °C	700 °C	0
2	PP	5:5	800 °C	700 °C	0
3	PS	5:5	800 °C	700 °C	0
4	HDPE	5:5	800 °C	700 °C	5 mL/h
5	PP	5:5	800 °C	700 °C	5 mL/h
6	PS	5:5	800 °C	700 °C	5 mL/h

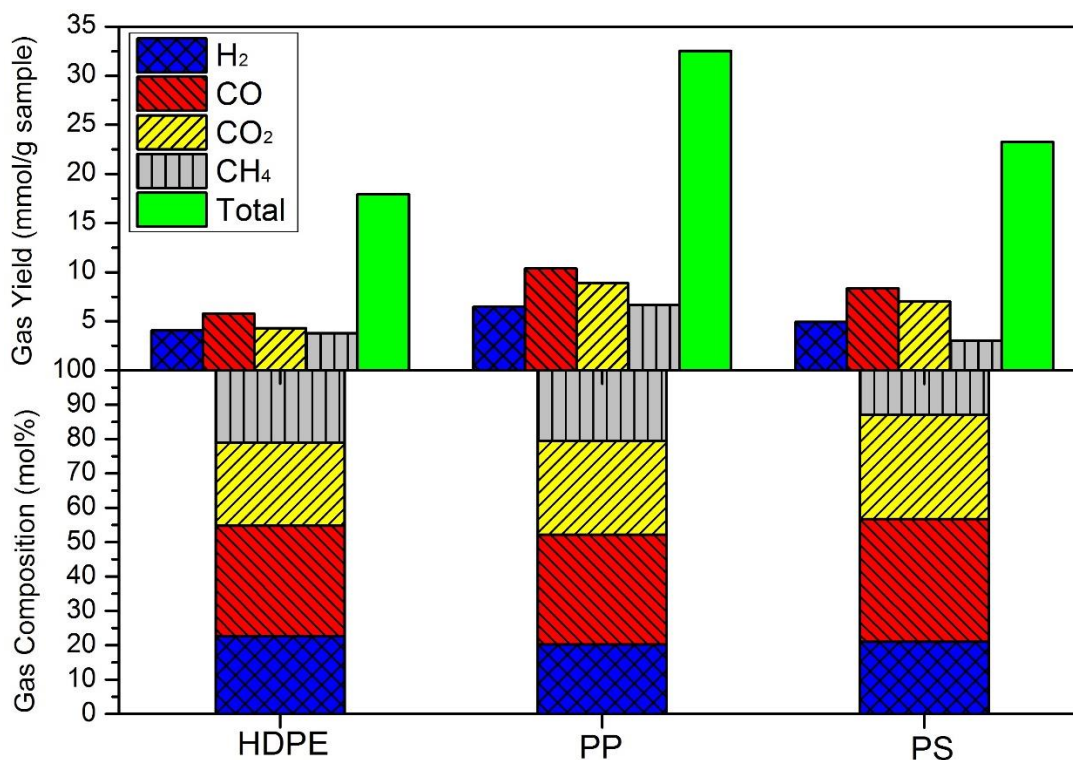
Experiment studies without catalyst were carried out first. The specific experiment plan is listed in Table 4. Only pyrolysis of biomass and plastics were performed. Specific gas yields and compositions are shown in Figure 5. Then, steam was introduced into system as gasification agent. The results of pyrolysis/gasification of biomass and plastics (without catalyst) are shown in Figure 6.



**Figure 5 Gas yields and compositions of pyrolysis of biomass and plastics**

(For all 3 cases: Plastic = 5:5, Pyrolysis T: 800 °C, Reforming T: 700 °C)

From Figure 5, when only pyrolysis of plastics and biomass takes place, gas yields are very low. The total gas yield of HDPE is 7.55 mmol/g, which is the lowest yield among three plastics. PS has a higher total gas yield at 12.74 mmol/g compared to HDPE, and PP has the highest total gas yield at 19.92 mmol/g. Four kinds of gas products are detected including H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>. The H<sub>2</sub> yields are not dominant and in very low amount, which are 0.72 mmol/g, 2.10 mmol/g and 1.10 mmol/g for HDPE, PP and PS respectively. The CO yields of HDPE, PP and PS are 2.88 mmol/g, 7.90 mmol/g and 5.78 mmol/g, which are much higher than that of H<sub>2</sub>. The CO<sub>2</sub> and CH<sub>4</sub> yields are lower than that of CO but higher than that of H<sub>2</sub>. As for the composition of gas products, CO accounts for the highest proportion (i.e. HDPE 37.97 mol%, PP 39.41 mol% and PS 45.21 mol%) and H<sub>2</sub> takes the lowest proportion (i.e. HDPE 9.79 mol%, PP 11.08 mol% and PS 8.74 mol%), which are consistent with the results of gas yields.



**Figure 6 Gas yields and compositions of pyrolysis/gasification of biomass and plastics (without catalyst)**

**(For all 3 cases: Plastic = 5:5, Pyrolysis T: 800 °C, Reforming: 700 °C, Water: 5 mL/h)**

From Figure 6, pyrolysis/gasification of plastics and biomass increases gas yields obviously after introduction of water as gasification agent. The total gas yield of PP is 32.51 mmol/g, which is higher than that of PS (23.35 mmol/g) and HDPE (17.94 mmol/g). The H<sub>2</sub> yields of HDPE, PP and PS are 4.06 mmol/g, 6.49 mmol/g and 4.92 mmol/g. Among three plastics, HDPE has the highest promotion on H<sub>2</sub> yield, which is over 5 times of that when only pyrolysis is carried out. CO yields are still very high compared to other gas products, which are 5.77 mmol/g (HDPE), 10.40 mmol/g (PP) and 8.34 mmol/g (PS). When it comes to the gas composition, H<sub>2</sub> compositions of three plastics increase to 22.65 mol% (HDPE), 20.21 mol% (PP) and 21.00 mol% (PS) due to rising amount of H<sub>2</sub> yields.

Compared to only pyrolysis, gasification introduces water as gasification agent, which allows the steam reforming reactions (i.e. Water-gas-shift (WGS) reaction and Steam-methane-reforming (SMR) reaction) to promote gas yield. Different categories of plastics have impacts on the gas yields and compositions obviously when mixing with biomass. PP has the highest

gas yields in both pyrolysis only and pyrolysis/gasification cases. This might be due to the highest alkane content generated from pyrolysis stage (demonstrated in *section 3.2*). Compared to alkene and aromatic, alkane is easier to be decomposed during cracking reactions. Alkene should absorb H radical first to be transferred into relevant saturated alkane, and then it can go on further cracking reactions. For aromatic, it is even more difficult to break the cycle structure of benzene, which consumes higher energy for cracking. It also needs to be noted that the CH<sub>4</sub> yields of PP in pyrolysis only and pyrolysis/gasification are higher than that of HDPE and PS. This is because that a great amount of methyl is released from PP, and the free methyl combines with H radical to form CH<sub>4</sub>. As for other plastics, it is surprised to observe that HDPE has the lowest gas yields in both pyrolysis only and pyrolysis/gasification situations. The gas yield of HDPE was predicted higher than that of PS before experiment. A probable explanation might be due to the synergic effect with biomass. According to Zhang et al. (2016), co-pyrolysis of biomass and plastics can influence and promote their individual decomposition interactively. Among three plastics, HDPE completes its pyrolysis process in the highest temperature range (see Figure 3). The synergic effect between HDPE and biomass is not so completed as that of PP and PS, resulting in insufficient decomposition of biomass. Consequently, the lowest gas yields are achieved by HDPE.

The specific H<sub>2</sub> yields and compositions of three plastics with biomass in pyrolysis only and pyrolysis/gasification are all not ideal. For HDPE, PP and PS with biomass, CO always takes the highest proportion and H<sub>2</sub> takes the lowest proportion of both yields and compositions for majority of time. It can be concluded that the important reactions to generate H<sub>2</sub> (e.g. WGS and SMR reactions) are in low reaction rates without acceleration of catalyst, which demonstrates the necessity of catalyst for H<sub>2</sub> production.

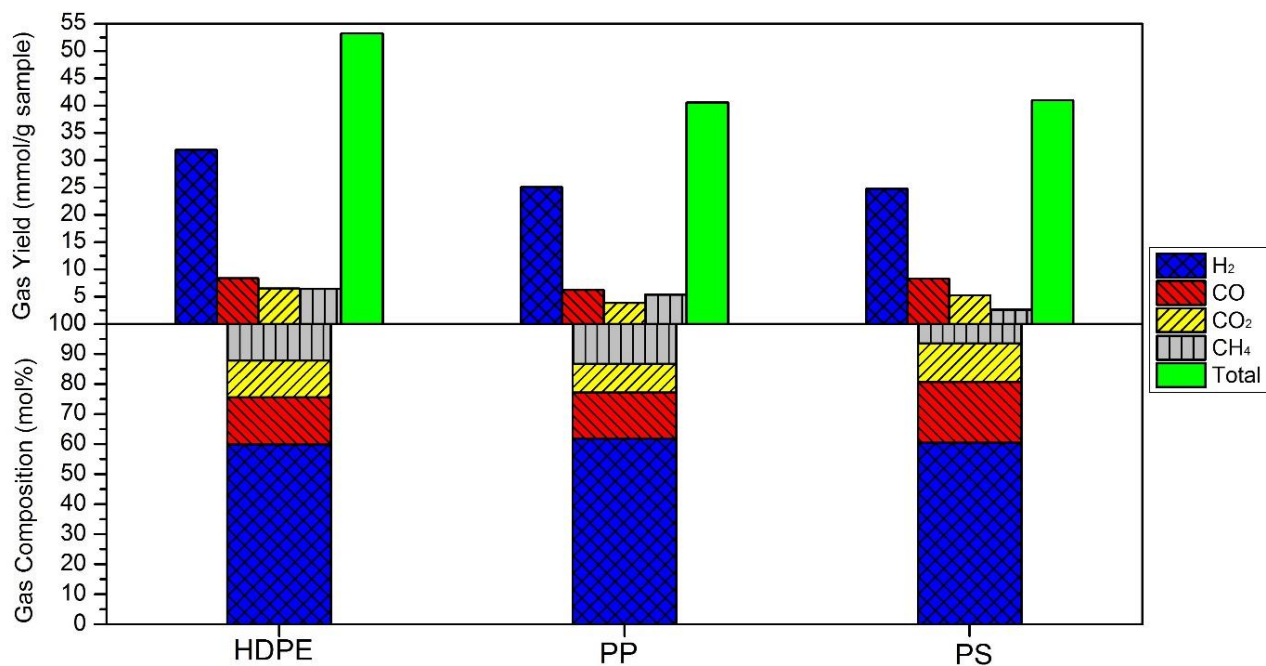
## 4.2 Pyrolysis/gasification of biomass and different plastics with catalyst

Experimental studies of pyrolysis/gasification of different plastics and biomass under Ni-Al<sub>2</sub>O<sub>3</sub> and new catalyst Ni-CaO-C were carried out. The specific experiment plan is shown in Table 5. The results of gas yields and compositions under Ni-Al<sub>2</sub>O<sub>3</sub> are shown in Figure 7. The results under new catalyst Ni-CaO-C are shown in Figure 8.

**Table 5 List of experiment studies for pyrolysis/gasification with catalyst**

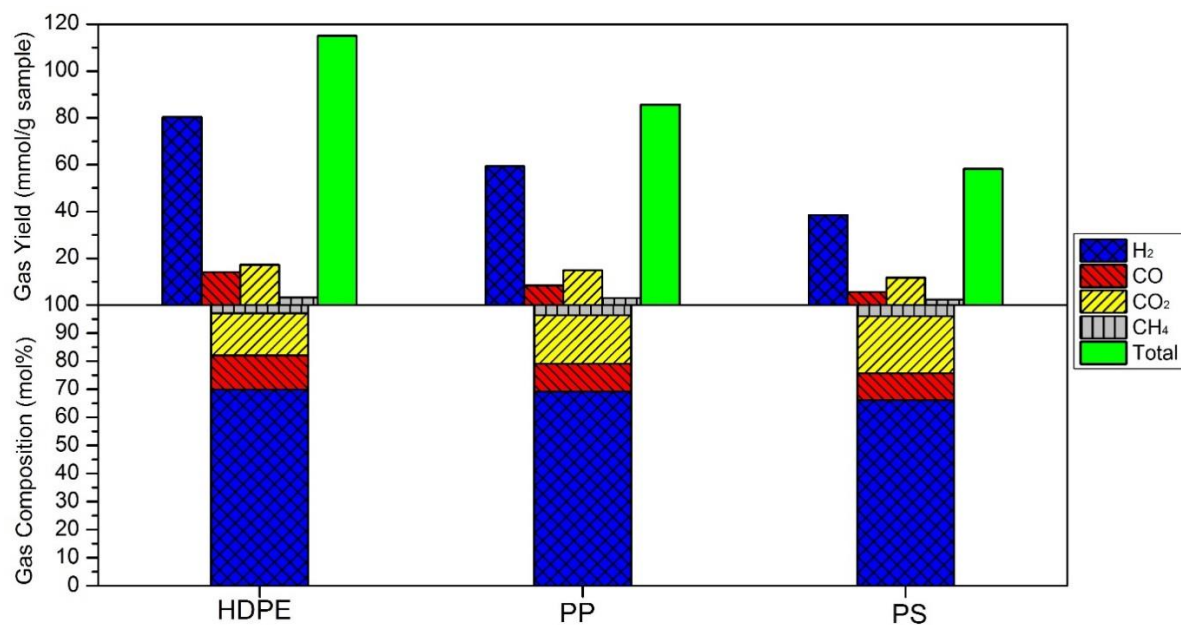
Exp.	Plastics	Feedstock ratio (Biomass: Plastics)	Pyrolysis T	Reforming T	Water injection	Catalyst
7	HDPE	5:5	800 °C	700 °C	5 mL/h	Ni-Al <sub>2</sub> O <sub>3</sub>
8	PP	5:5	800 °C	700 °C	5 mL/h	Ni-Al <sub>2</sub> O <sub>3</sub>
9	PS	5:5	800 °C	700 °C	5 mL/h	Ni-Al <sub>2</sub> O <sub>3</sub>
10	HDPE	5:5	800 °C	700 °C	5 mL/h	Ni-CaO-C
11	PP	5:5	800 °C	700 °C	5 mL/h	Ni-CaO-C
12	PS	5:5	800 °C	700 °C	5 mL/h	Ni-CaO-C

From Figure 7, a great increase of gas yields is observed after introducing catalyst Ni-Al<sub>2</sub>O<sub>3</sub>. Among three plastics with biomass, the promotion effect of catalyst on products yields of HDPE is most obvious. HDPE has the highest total gas yield at 53.26 mmol/g followed by the yields of PS and PP at 40.99 mmol/g and 40.58 mmol/g respectively. Compared to the experimental studies without catalyst, H<sub>2</sub> production including both H<sub>2</sub> yield and composition is promoted significantly. The H<sub>2</sub> yields of HDPE, PP and PS are 31.87 mmol/g, 25.08 mmol/g and 24.76 mmol/g. The H<sub>2</sub> compositions for three plastics are 59.84 mol% (HDPE), 61.79 mol % (PP) and 60.41 mol% (PS), which are all more than half of total proportion. For other gas products, yields and compositions of CO are still higher than that of CO<sub>2</sub> and CH<sub>4</sub> for three plastics.



**Figure 7 Gas yields and compositions of pyrolysis/gasification of biomass and plastics under catalyst Ni-Al<sub>2</sub>O<sub>3</sub>**

(For all 3 cases: Biomass: Plastic = 5:5, Pyrolysis T: 800 °C, Reforming: 700 °C, Water: 5 mL/h)



**Figure 8 Gas yields and compositions of pyrolysis/gasification of biomass and plastics under catalyst Ni-CaO-C**

(with all Biomass: Plastic = 5:5, Pyrolysis T: 800 °C, Reforming: 700 °C, Water: 5 mL/h)

From Figure 8, it can be observed that new catalyst Ni-CaO-C has better performance to promote gas yields and compositions than Ni-Al<sub>2</sub>O<sub>3</sub>. The total gas yields of HDPE, PP and PS are 115.04 mmol/g, 85.68 mmol/g and 58.26 mmol/g respectively. HDPE still has the highest total gas yields under catalyst Ni-CaO-C. The specific yields of H<sub>2</sub> are all in high levels for three plastics. For HDPE, the H<sub>2</sub> yield is 80.36 mmol/g. A medium H<sub>2</sub> yield at 59.35 mmol/g is observed by PP, and PS has the lowest H<sub>2</sub> yield at 38.51 mmol/g. The yields of CO and CO<sub>2</sub> rise slightly for three plastics compared to that under Ni-Al<sub>2</sub>O<sub>3</sub>. However, the CH<sub>4</sub> yields of HDPE, PP and PS decrease from 6.45 mmol/g, 5.39 mmol/g and 2.67 mmol/g (using Ni-Al<sub>2</sub>O<sub>3</sub>) to 3.35 mmol/g, 3.05 mmol/g and 2.33 mmol/g (using Ni-CaO-C). This might be due to promotion of SMR reaction, which consumes CH<sub>4</sub> to generate more H<sub>2</sub>. As for the gas compositions, the CO<sub>2</sub> compositions are 15.00 mol% (HDPE), 17.39 mol% (PP) and 20.28 mol% (PS), which are slightly higher than that under Ni-Al<sub>2</sub>O<sub>3</sub>. However, the H<sub>2</sub> compositions still takes the highest proportion at 69.86 mol% (HDPE), 69.21 mol% (PP) and 66.09 mol% (PS), which are all higher than the H<sub>2</sub> compositions under Ni-Al<sub>2</sub>O<sub>3</sub>.

The good catalytic ability of new catalyst Ni-CaO-C to promote H<sub>2</sub> production (with high H<sub>2</sub> yield and composition) from pyrolysis/gasification of different plastics (i.e. HDPE, PP and PS) with biomass can be demonstrated. The specific H<sub>2</sub> yields and compositions of different studies are shown in Table 6.

**Table 6 H<sub>2</sub> yields and compositions of pyrolysis/gasification of different plastics with biomass in different studies**

Plastics	Pyrolysis only without catalyst		Pyrolysis/gasification without catalyst		Pyrolysis/gasification under Ni-Al <sub>2</sub> O <sub>3</sub>		Pyrolysis/gasification under Ni-CaO-C	
	Yield (mmol/g)	Composition (mol%)	Yield (mmol/g)	Composition (mol%)	Yield (mmol/g)	Composition (mol%)	Yield (mmol/g)	Composition (mol%)
HDPE	0.72	9.79	4.06	22.65	31.87	59.84	80.36	69.86
PP	2.20	11.08	6.49	20.21	25.08	61.79	59.35	69.21
PS	1.10	8.74	4.92	21.00	24.76	60.41	38.51	66.09

From Table 6, introduction of catalyst helps to increase H<sub>2</sub> yields and compositions significantly for three plastics with biomass. This demonstrates the necessity of catalyst to promote H<sub>2</sub> production. Compared to traditional Ni-Al<sub>2</sub>O<sub>3</sub> catalyst, new catalyst Ni-CaO-C has better performance of H<sub>2</sub> production under the same operating conditions. Ni-CaO-C has the best promotion effect on HDPE with biomass and the H<sub>2</sub> yield and composition increase by 48.49 mmol/g (from 31.87 to 80.36 mmol/g) and 10.02 mol% (from 59.84 to 69.86 mol%) compared to Ni-Al<sub>2</sub>O<sub>3</sub>. The least promotion effect of Ni-CaO-C is observed on PS, whose H<sub>2</sub> yield increases by 13.75 mmol/g (from 24.76 to 38.51 mmol/g) and H<sub>s</sub> composition increases by 5.68 mol% (from 60.41 to 66.09 mol%). The probable reasons might be that the different physical and chemical properties of plastics not only influence the synergic effects between plastics and biomass, but also results in diversities of performance under catalyst Ni-CaO-C. The specific differences of plastics and biomass under catalyst Ni-CaO-C will be analysed in the following section.

### **4.3 Mechanism of catalyst Ni-CaO-C catalysing different plastics and biomass**

#### **4.3.1 Working principle of catalyst Ni-CaO-C**

First of all, the general working principle of Ni-CaO-C to catalyse pyrolysis/gasification of plastics and biomass is introduced (see Figure 9). Co-pyrolysis of plastics and biomass takes place at the top stage inside the two-stage fixed bed reactor. Plastics is rich in hydrogen content and decomposition of plastics release a large amount of H radical. Generated free H radical has various function: (i) Combining with free methyl to form CH<sub>4</sub>; (ii) Combining with alkene to saturate unsaturated structure; (iii) Combining with another H radical to form H<sub>2</sub>; (iv) More importantly, combining with radicals released from biomass to promote cracking of biomass (Zhang et al., 2016). Consequently, products including char and volatiles are generated after decomposition of plastics and biomass. The generated char is left in the quartz crucible (Figure 2, *symbol 5*). Only volatiles and gasification agent water (in the form of steam) are transferred

into the bottom reforming stage with carrier gas N<sub>2</sub>. According to the results of TG-FTIR analysis (see Figure 4 in *section 3*), the compositions of volatiles entering the bottom stage are different for different plastics with biomass. When volatiles contact with the catalyst layer, the catalyst Ni-CaO-C functions to catalyse series of relevant reactions for a higher H<sub>2</sub> production. The synergic effect between Ni, activated carbon and CaO are shown below. Typical reactions occurring in the reforming stage are also listed below (Abdelouahed et al., 2012; Yan et al., 2020).

**Water – Gas Reaction :**



**Boudouard Reaction :**



**Methanation Reaction :**



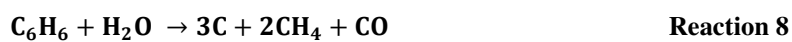
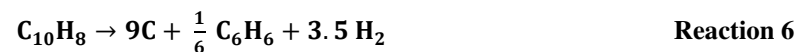
**Water-Gas-Shift Reaction:**



**Steam-Methane-Reforming Reaction:**



**Typical cracking reactions:**



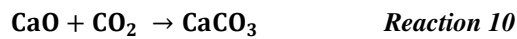
As the active core of catalyst, Ni/NiO is used to accelerate the reactions (e.g. reforming reactions and cracking reactions) by reducing activation energy. Reforming reactions including WGS (*Reaction 4*) and SMR (*Reaction 5*) reactions are good at generating more H<sub>2</sub>. Cracking reactions helps to further convert high molecular weight hydrocarbons into low molecular

weight ones (*Reactions 6 - 9*). In addition, as the gasification agent, water also could release free radicals in reforming stage. These generated radicals are adsorbed by catalyst and contact with volatiles from pyrolysis stage, which promotes cracking of tar into CO and H<sub>2</sub> under the help of active core on catalyst surface (Claude et al., 2016).

As one catalyst support, activated carbon has the following advantages in improving H<sub>2</sub> production: (i) Activated carbon is active to participate in reactions (*Reaction 1 -3*) in reforming stage. H<sub>2</sub> and CO are generated through Water-Gas reaction (WG) (*Reaction 1*), which increases H<sub>2</sub> yield directly. Yields of CO and CH<sub>4</sub> are promoted through Boudouard reaction (*Reaction 2*) and Methanation reaction (*Reaction 3*). The increasing CO and CH<sub>4</sub> could help to move the equilibriums of WGS and SMR reactions towards generating more H<sub>2</sub> due to increasing concentration of reactants. (ii) Activated carbon has good pore structure as catalyst support, which possesses large specific surface area (Pandey et al., 2015). On one hand, abundant active core Ni is possible to be loaded. On the other hand, sufficient inner space can be provided for catalytic reactions such as cracking and reforming reactions. As a result, the total gas yields (including H<sub>2</sub>) could be promoted. (iii) Activated carbon itself has perfect reduction ability. In catalyst preparation stage, the active core NiO could be reduced to form Ni during calcination. Compared to NiO, Ni has better catalytic activity, which increases the gas yields to a large extent (Alnarabiji et al., 2019).

As the second catalyst support, CaO has great CO<sub>2</sub> adsorption capability. The principle how CaO adsorbs CO<sub>2</sub> is shown in *Reaction 10*. When volatiles contact with Ni-CaO-C, generated CO<sub>2</sub> is adsorbed by CaO. In this way, CO<sub>2</sub> composition in gas products decreases, which increases compositions of other gas products (including H<sub>2</sub>) straightforward. In addition, the decreasing CO<sub>2</sub> concentration could help to move the equilibrium of WGS reaction towards generating more CO<sub>2</sub> and H<sub>2</sub>. Newly generated CO<sub>2</sub> can be adsorbed by CaO again until the CaO is saturated. In this way, the H<sub>2</sub> composition is promoted. It should be noted that the CO<sub>2</sub>

compositions under Ni-CaO-C (Figure 8) are slightly higher than that under Ni-Al<sub>2</sub>O<sub>3</sub> (Figure 7). This is probably because Ni-CaO-C has much better catalytic ability than Ni-Al<sub>2</sub>O<sub>3</sub> to increase the total gas yields and the increasing CO<sub>2</sub> exceeds the adsorption limit of CaO. Even though CO<sub>2</sub> adsorption exists, the CO<sub>2</sub> composition is still higher than that under Ni-Al<sub>2</sub>O<sub>3</sub>. It is also believed that the CO<sub>2</sub> composition could reach even higher levels if without CaO component.



In summary, Ni and activated carbon have an obvious influence to increase the total gas yields, thus H<sub>2</sub> yield is promoted effectively. The H<sub>2</sub> composition could increase with rising H<sub>2</sub> yield, but the yields of other gas products also increase simultaneously, which offsets the enhancement of H<sub>2</sub> composition. Compared to Ni and activated carbon, CaO serves to adsorb the booming CO<sub>2</sub> composition and promote WGS reaction in purpose. In this way, the three components of the Ni-CaO-C synergise to promote the H<sub>2</sub> yield and composition.

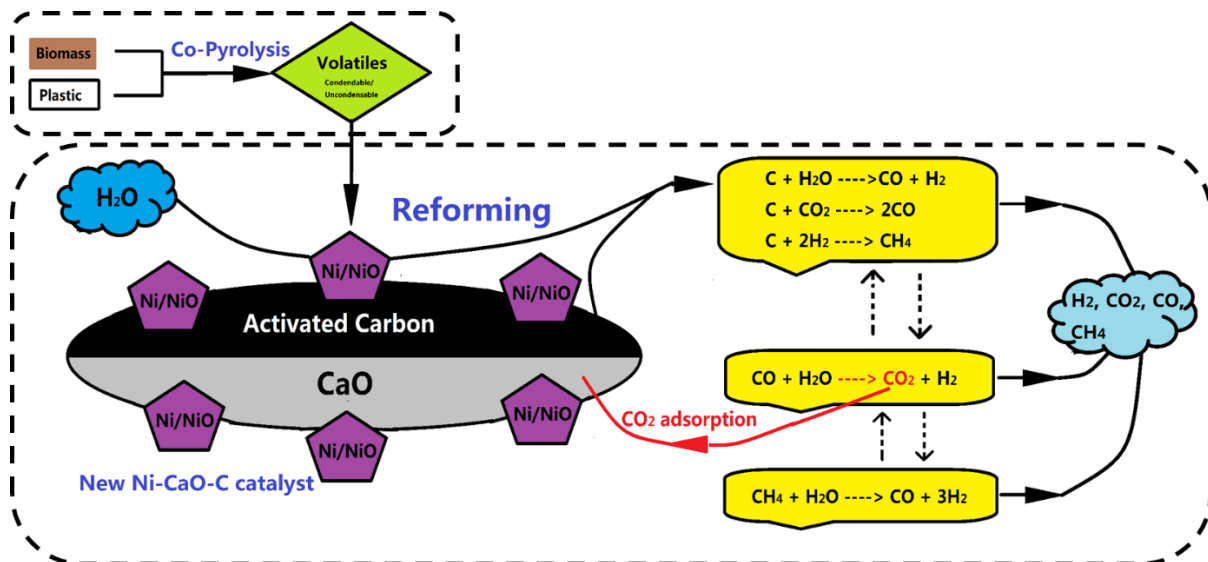


Figure 9 Mechanism of Ni-CaO-C during pyrolysis/gasification of plastic and biomass

(adapted from Kumagai et al., 2015)

#### 4.3.2 Influence of different types of plastics on performance of catalyst Ni-CaO-C

When it comes to the specific differences in H<sub>2</sub> production of three plastics with biomass, it can be observed that HDPE benefits most after introduction of catalyst. From Table 6, PP has

the highest H<sub>2</sub> yield and composition when no catalyst is used for pyrolysis only and pyrolysis/gasification of plastics and biomass. This is because the high methyl content of PP results in high alkane yield, which has been explained in *section 4.1*. After introduction of catalysts, H<sub>2</sub> yields and compositions of HDPE under Ni-Al<sub>2</sub>O<sub>3</sub> and Ni-CaO-C all exceed that of PP. Compared to experiments under Ni-Al<sub>2</sub>O<sub>3</sub>, HDPE also has the highest H<sub>2</sub> yield and composition increase (increase by 48.49 mmol/g and 10.02 mol%) when Ni-CaO-C is used. To explain the phenomena, the volatiles of pyrolysed PP has more CH<sub>4</sub> compared to that of HDPE. Therefore, SMR reaction is dominant when volatiles from PP go through reforming stage and WGS reaction is dominant when volatiles from HDPE go through reforming stage.

(a) Catalyst Ni-CaO-C is more effective to decrease the activation energy of reactions in reforming stage for HDPE than that of PP. According to Abbas et al. (2017), activation energy of SMR reaction is much higher than that of WGS reaction. Under the function of catalyst Ni-CaO-C, the activation energy of WGS reaction is easier to be decreased to a lower level compared to SMR reaction. In this way, WGS reaction is promoted more effectively. Consequently, the H<sub>2</sub> yield and composition of HDPE are promoted to higher levels.

(b) From thermodynamics aspect, SMR reaction is endothermic and WGS reaction is exothermic. The same reforming temperature at 700 °C might be favourable to WGS but unfavourable to SMR. Better H<sub>2</sub> yield and composition might be obtained under higher reforming temperatures.

Compared to HDPE and PP, the aromatic structure of PS requires higher energy to be totally decomposed in pyrolysis stage and more high molecular weight volatiles are transferred to reforming stage. Even under the catalyst Ni-CaO-C, more catalytic capability of catalyst is used to promote cracking reactions (*Reactions 6 - 9*) rather than reforming reactions to generate H<sub>2</sub>. This restricts H<sub>2</sub> production effectively. To summarise, the effects of Ni-CaO-C to catalyse

co-pyrolysis/gasification of plastics and biomass for H<sub>2</sub> production rank in the sequence HDPE>PP>PS.

### 5. Influence of operating conditions on H<sub>2</sub> production under catalyst Ni-CaO-C

After demonstrating the catalytic activity of catalyst Ni-CaO-C for co-pyrolysis/gasification of different plastics with biomass, the influences of operating conditions on H<sub>2</sub> production under catalyst Ni-CaO-C were also investigated. The specific experiment plan is listed in Table 7:

**Table 7 List of experiment studies for pyrolysis/gasification under catalyst Ni-CaO-C**

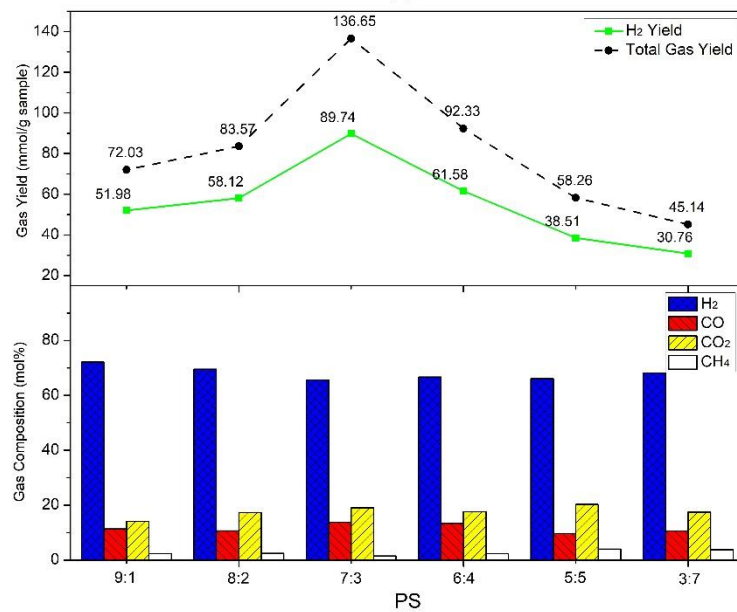
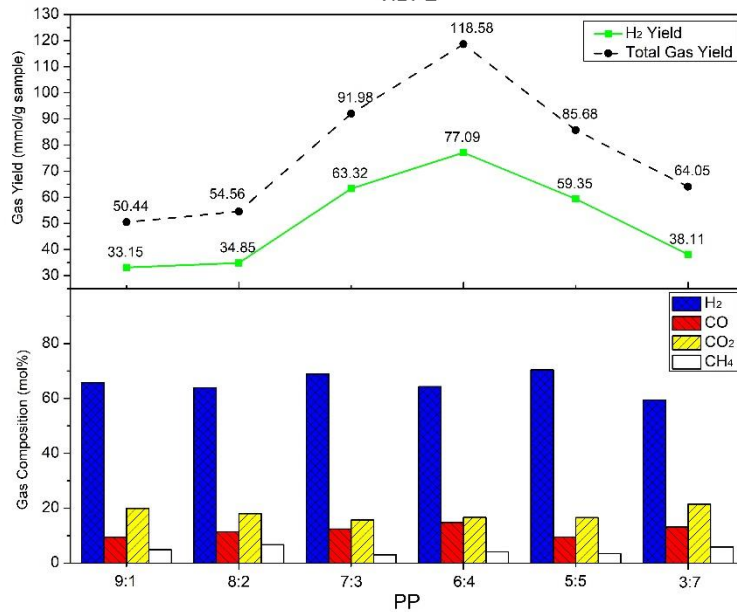
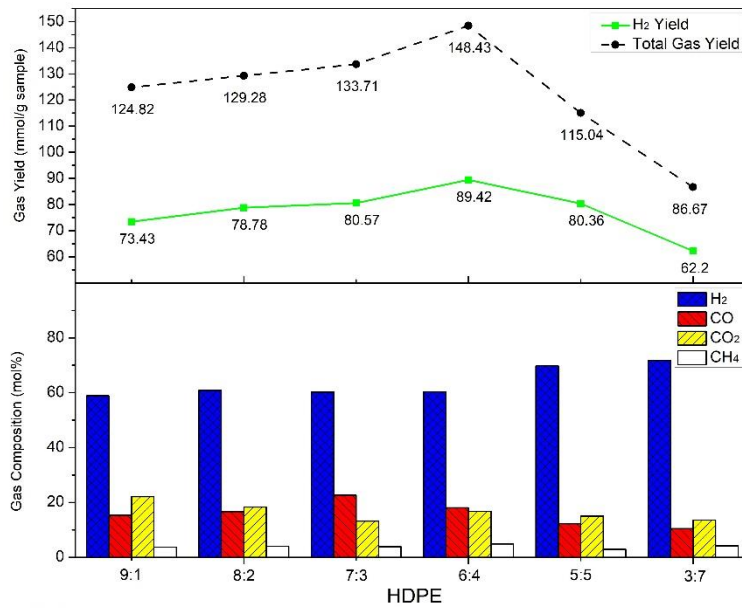
Exp.	Plastics	Feedstock ratio (Biomass: Plastics)	Pyrolysis T	Reforming T	Water injection
13	HDPE	9:1	800 °C	700 °C	5 mL/h
14	HDPE	8:2	800 °C	700 °C	5 mL/h
15	HDPE	7:3	800 °C	700 °C	5 mL/h
16	HDPE	6:4	800 °C	700 °C	5 mL/h
17	HDPE	3:7	800 °C	700 °C	5 mL/h
18	PP	9:1	800 °C	700 °C	5 mL/h
19	PP	8:2	800 °C	700 °C	5 mL/h
20	PP	7:3	800 °C	700 °C	5 mL/h
21	PP	6:4	800 °C	700 °C	5 mL/h
22	PP	3:7	800 °C	700 °C	5 mL/h
23	PS	9:1	800 °C	700 °C	5 mL/h
24	PS	8:2	800 °C	700 °C	5 mL/h
25	PS	6:4	800 °C	700 °C	5 mL/h
26	PS	7:3	800 °C	700 °C	5 mL/h
27	PS	3:7	800 °C	700 °C	5 mL/h
28	HDPE	5:5	800 °C	600 °C	5 mL/h
29	HDPE	5:5	800 °C	800 °C	5 mL/h
30	PP	5:5	800 °C	600 °C	5 mL/h
31	PP	5:5	800 °C	800 °C	5 mL/h
32	PS	5:5	800 °C	600 °C	5 mL/h
33	PS	5:5	800 °C	800 °C	5 mL/h
34	HDPE	5:5	800 °C	700 °C	1 mL/h
35	HDPE	5:5	800 °C	700 °C	10 mL/h

36	PP	5:5	800 °C	700 °C	1 mL/h
37	PP	5:5	800 °C	700 °C	10 mL/h
38	PS	5:5	800 °C	700 °C	1 mL/h
39	PS	5:5	800 °C	700 °C	10 mL/h

### 5.1 Influence of feedstock ratio on H<sub>2</sub> production

Feedstock ratio of plastics and biomass can influence their synergic effect under the new catalyst Ni-CaO-C. The results of changing feedstock ratios influencing H<sub>2</sub> production are shown in Figure 10. When it comes to the gas yield, it can be observed that when 10 wt% HDPE (Biomass : Plastics = 9:1) is contained in feedstock, total gas yield and H<sub>2</sub> yield are 124.82 mmol/g and 73.43 mmol/g respectively. With plastics content increase, gas production keeps increasing until the highest total gas yield and H<sub>2</sub> yield are achieved at 40 wt% HDPE with 148.43 mmol/g and 89.42 mmol/g. Then, H<sub>2</sub> yield decreases to 80.36 mmol/g and the total gas yield decreases significantly to 115.04 mmol/g with 50 wt% HDPE in feedstock. Eventually, lower total gas yield and H<sub>2</sub> yield are observed at 86.67 mmol/g and 62.2 mmol/g when 70 wt% HDPE is used in the feedstock. Similarly, the gas yield of PP and PS have similar trends compared to that of HDPE. The total gas yield and H<sub>2</sub> yield of PP increase from 10 wt% PP (50.44 mmol/g and 33.15 mmol/g) to 40 wt% PP (118.58 mmol/g and 77.09 mmol/g) in feedstock. Further increase of PP content results in continuous decrease of gas production and the total gas yield and H<sub>2</sub> yield at 70 wt% PP are 64.05 mmol/g and 38.11 mmol/g. For PS, the point with the highest gas production is different from that of HDPE and PP (i.e. at 40 wt% plastics content), which is achieved at 30 wt% PS with 136.65 mmol/g total gas yield and 89.74 mmol/g H<sub>2</sub> yield. In summary, with plastic content increase in feedstock, both total gas yield and H<sub>2</sub> yield increase at first but decrease eventually after certain plastics content. As for the gas composition, the H<sub>2</sub> compositions of three plastics under different plastics are changeable without obvious trends. However, majority of the H<sub>2</sub> compositions are at relatively high level, which are all higher than 60 mol%.

Before experiments, it was predicted that increasing plastic content in feedstock would be helpful to raise the H<sub>2</sub> yield since the high H/C ratio of plastic could improve the H<sub>2</sub> formation by providing more H radical. In the studies of Pinto et al. (2002) and Alvarez et al. (2014), the increasing plastic content (up to 20 wt%) in mixture of feedstock (plastics mixing with biomass) is advantageous to promote the H<sub>2</sub> yield. However, it is surprising and interesting to conclude from Figure 10 that all the three plastics show similar decreasing trends of H<sub>2</sub> yield after increasing the plastic content from certain value (40 wt% for HDPE and PP; 30 wt% for PS). Actually, similar results of decreasing H<sub>2</sub> yield were also achieved from studies of Lopez et al. (2015), Burra and Gupta (2018), Xu et al., (2019) and our previous study (Chai et al., 2019). In the study of Lopez et al., they investigated the co-pyrolysis/gasification of HDPE (0 – 100 wt%) and biomass under steam atmosphere. A decreasing H<sub>2</sub> production was observed when the HDPE content was higher than 50 wt%. In the study of Burra and Gupta, three different plastics (PP, PET and BPC) were individually mixed with biomass for pyrolysis/gasification. When the plastic content of three plastics were all higher than 60 wt%, the H<sub>2</sub> yield all started to decrease. In our previous study, the H<sub>2</sub> yield also decreased when LDPE is higher than 50 wt% in feedstocks. Therefore, it seems that the probable plastics limit might be around 30 wt% ~ 40 wt% for biomass and plastics mixture. When plastics is higher than these limit, decreasing trends of H<sub>2</sub> yield could be resulted considering the results in aforementioned studies and in this study.



Feedstock Ratio (Biomass:Plastic, wt%)

### **Figure 10 Gas composition and yield when changing feedstock ratio**

**(For all cases under catalyst Ni-CaO-C, Pyrolysis T: 800 °C, Reforming T: 700 °C, Water: 5 mL/h)**

The proper explanation of decreasing H<sub>2</sub> yield might be due to reaching the limit of synergic effect between biomass and plastics. Plastics could provide abundant H radical during pyrolysis to promote H<sub>2</sub> formation. In addition, H radical could also react with radicals from biomass to promote cracking of complicated hydrocarbons (e.g. aromatics) and lighter hydrocarbons and CO (Abdelouahed et al., 2012) are generated. Then, H<sub>2</sub>O as another H element resource will be consumed to react with generated lighter hydrocarbons and CO through reforming reactions to promote total gas yield (including H<sub>2</sub> yield) furthermore. This is consistent with the higher total gas yield and H<sub>2</sub> yield when more biomass is in feedstock (Figure 10). To summarise, assuming the total amount of biomass and plastics is constant and here takes HDPE as example. Increasing HDPE content under specific range (less than 40 wt%) can promote the H<sub>2</sub> yield due to increasing H/C (resulting by increasing plastics). However, excessive HDPE content (higher than 40 wt%) in feedstock starts to hinder the amount of released radicals from biomass, which restricts further reforming reactions to improve total gas yield and H<sub>2</sub> yield.

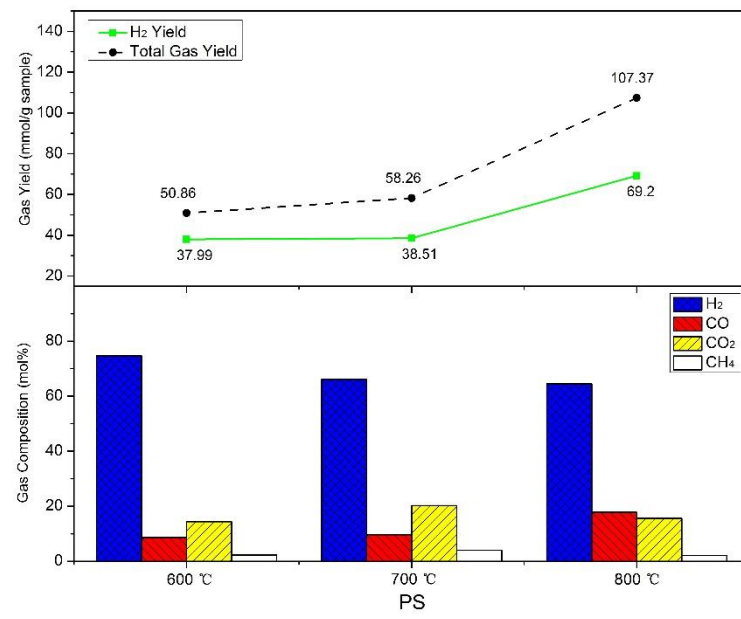
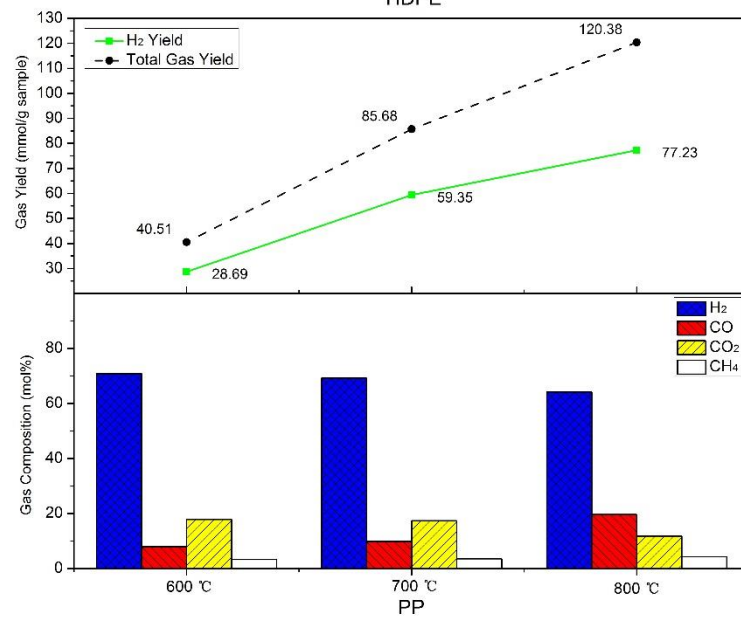
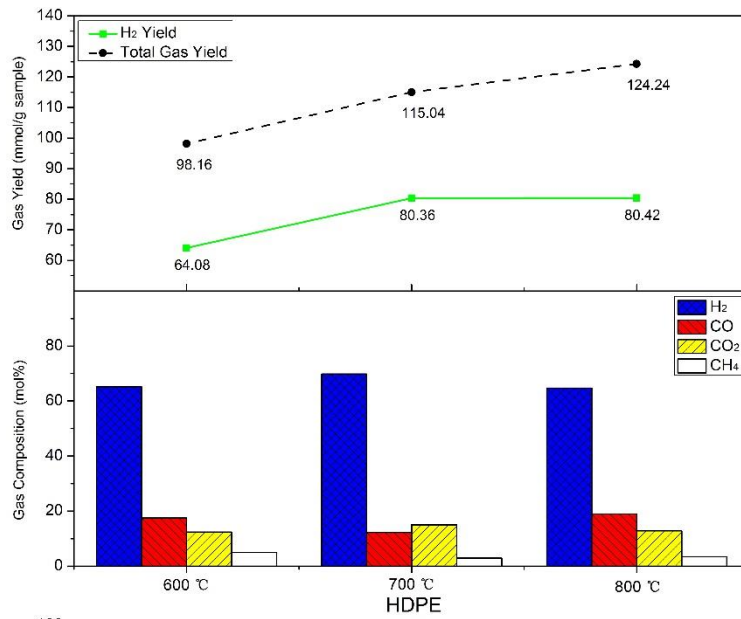
Again from Figure 10, among the three plastics tested, HDPE has the lowest H<sub>2</sub> yield reduction at 27.22 mmol/g (89.42 to 62.20 mmol/g) and PS has the highest H<sub>2</sub> yield reduction at 58.98 mmol/g (from 89.74 to 30.76 mmol/g) when plastics increases from 10 wt% to 70 wt%. This suggests that HDPE is more suitable to be mixed with biomass for pyrolysis/gasification under a higher plastic content compared PS and PP, which could be used as instruction for future industrial application.

### **5.2 Influence of reforming temperature on H<sub>2</sub> production**

Temperature is an important factor influencing the catalytic activity of catalyst and reaction rate of reactions in reforming stage. The results of reforming temperature influencing gas yield and composition under catalyst Ni-CaO-C are shown in Figure 11. From Figure 11, the H<sub>2</sub> yield of HDPE at 600 °C is 64.08 mmol/g. With temperature increase, H<sub>2</sub> yields of HDPE are

80.36 mmol/g at 700 °C and 80.42 mmol/g at 800 °C. For PP, the H<sub>2</sub> yield gradually increases from 28.69 mmol/g (at 600 °C) to 59.35 mmol/g (at 700 °C) and then to 77.23 mmol/g (at 800 °C). For PS, only a slight increase of H<sub>2</sub> yield is observed from 37.99 mmol/g to 38.51 mmol/g between 600 °C and 700 °C, but an obvious increase of H<sub>2</sub> yield is further observed to 69.20 mmol/g when temperature increases to 800 °C. For all three kinds of plastics, the total gas yields keep increasing with increase of temperature. The H<sub>2</sub> composition in product gas from different plastics changes slightly without specific trend. However, the H<sub>2</sub> compositions under different temperatures are all higher than 60 mol%.

It can be concluded that higher temperature is advantageous for improving the H<sub>2</sub> yield. This finding is consistent with results from previous studies (Pinto et al., 2003; Brachi et al., 2014; Erkiaga et al., 2014). According to thermodynamics, Water – Gas reaction (*Reaction 1*), Boudouard reaction (*Reaction 2*) and SMR reaction (*Reaction 5*) are all endothermic reactions, whose reaction equilibriums move towards generating more products under higher temperature. Therefore, the total gas yields are promoted. H<sub>2</sub> yield can be promoted at the same time. According to kinetic dynamics, reaction rates are accelerated under higher temperature, promoting reaction extent to produce more products.



Reforming Temperature (°C)

### Figure 11 Gas composition and yield when changing reforming temperature

(For all cases under catalyst Ni-CaO-C, Biomass: Plastic = 5:5, Pyrolysis T: 800 °C, Water: 5 mL/h)

From Figure 11, among three plastics, temperature has different effects to influence H<sub>2</sub> yield under catalyst Ni-CaO-C. For PP, with temperature increase, the promotion effect on H<sub>2</sub> yield at 700 °C and 800 °C are similar. At 700 °C, the performance of Ni-CaO-C to catalyse HDPE is ideal enough for H<sub>2</sub> production because further increase of temperature only has slight increase on H<sub>2</sub> yield. On the contrary, the H<sub>2</sub> yields of PS at 600 °C and 700 °C are both at relatively low level, but the H<sub>2</sub> yield increases significantly at 800 °C. This might be due to more complicated structure of PS compared to other plastics (HDPE and PP) and higher temperature at 800 °C could ensure sufficient breakdown the aromatics in PS for reforming reactions. In summary, assuming catalyst Ni-CaO-C can be applied for practical use in future, adequately high temperature is necessary for PS to ensure lowest acceptable H<sub>2</sub> yield. For PP, the temperature is suggested to be as high as possible to realise possible H<sub>2</sub> yield. For HDPE, 700 °C is enough to make the most use of the catalytic activity of catalyst Ni-CaO-C for H<sub>2</sub> production.

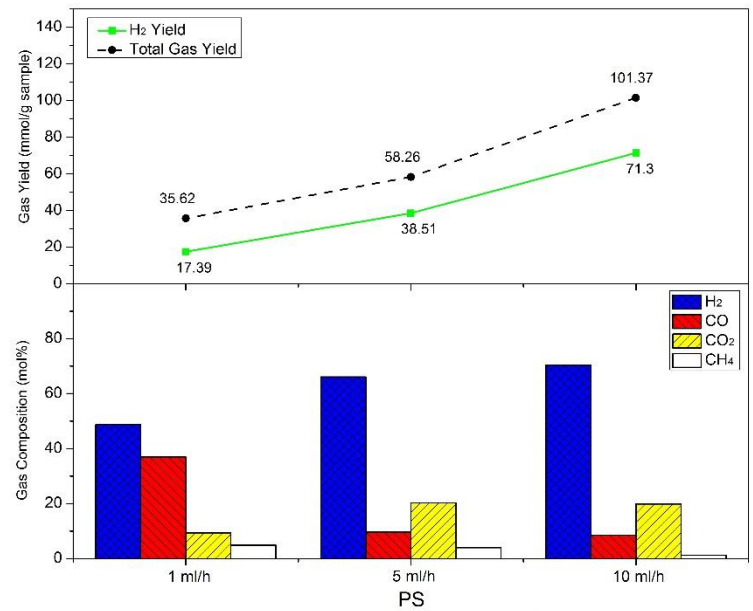
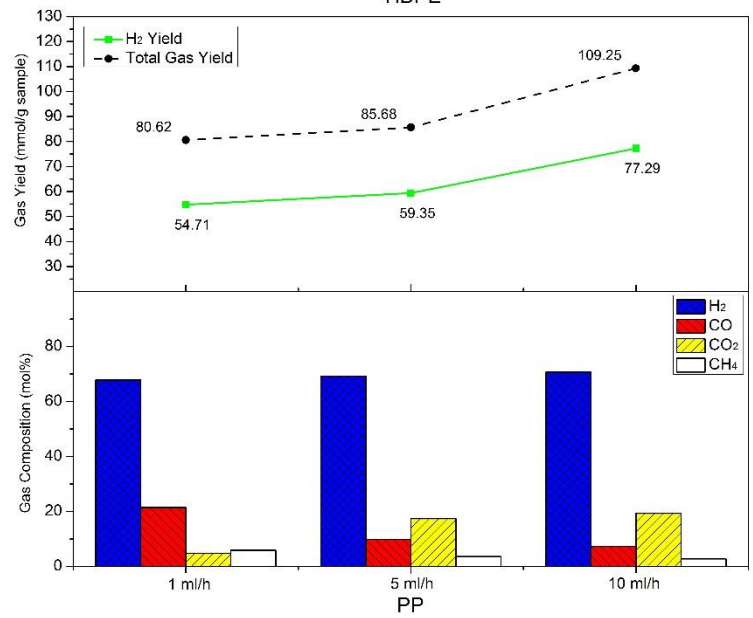
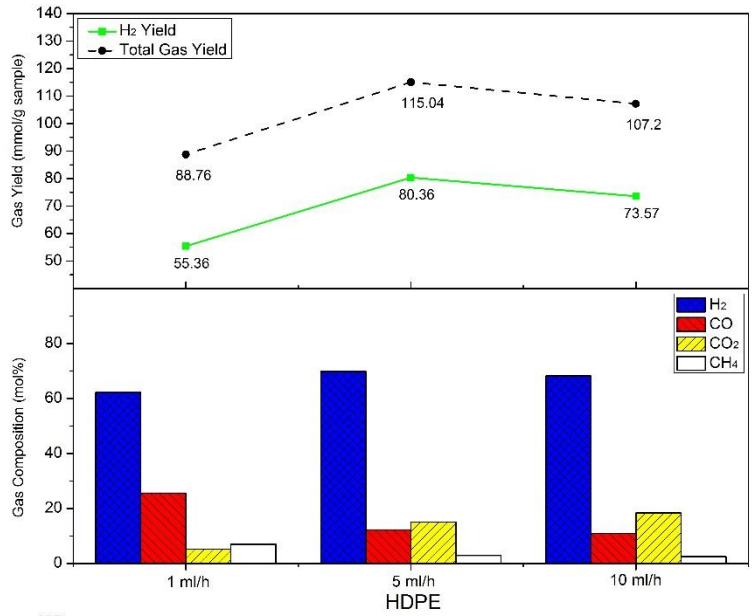
### 5.3 Influence of water injection flowrate on H<sub>2</sub> production

As gasification agent, amount of water injection into system can influence the progress of reforming reactions under catalyst Ni-CaO-C. The results of gas yield and composition changing with water injection flowrate are shown in Figure 12. From Figure 12, the H<sub>2</sub> yield of HDPE increases from 55.36 mmol/g to 80.36 mmol/g when water injection flowrate increases from 1 mL/h to 5 mL/h. Then the H<sub>2</sub> yield decreases to 73.57 mmol/g when water injection increases to 10 mL/h. The changing trend of H<sub>2</sub> composition of HDPE is similar as H<sub>2</sub> yield, which firstly increases to 69.86 mol% at 5 mL/h and then decreases to 68.22 mol% at 10 mL/h. For PP, the H<sub>2</sub> yield keeps increasing from 54.71 mmol/g at 1 mL/h to 77.29 mmol/g at 10 mL/h. For PS, the H<sub>2</sub> yield keeps increasing from 17.39 mmol/g at 1 mL/h to 71.30 mmol/g at 10 mL/h. The H<sub>2</sub> compositions when using PP and PS all keeps increasing

with the increase of water injection flowrate, and the highest H<sub>2</sub> compositions are 70.61 mol% (PP) and 70.34 mol% (PS) at 10 mL/h respectively.

It can be observed that except for HDPE, the higher water injection flowrate can result in higher H<sub>2</sub> yield and composition. This is because that introduction of more gasification agent (i.e. H<sub>2</sub>O) into system could promote WGS reaction (*Reaction 4*), whose reaction equilibrium moves towards generating more H<sub>2</sub>. In this study, it is suggested to treat these two plastics under as high as water injection flowrate under catalyst Ni-CaO-C for PP and PS. However, excessive water injected into the reactor could hinder H<sub>2</sub> production on the contrary. For HDPE, 10 mL/h water injection decreases H<sub>2</sub> yield and composition eventually compared to PP and PS. According to Li et al. (2012), considerable latent heat could be absorbed by excessive water inside the reactor. This can hinder sufficient decomposition of feedstock in pyrolysis stage and smooth progress of endothermic reactions in reforming stage, thus restricting H<sub>2</sub> production. Therefore, the water injection flowrate for HDPE is suggested to be controlled at an intermediate level under Ni-CaO-C to save water resource and keep H<sub>2</sub> production acceptable.

From Figure 12, among three plastics, PS is most sensitive to water injection flowrate change. Compared to HDPE and PP, the H<sub>2</sub> yield and H<sub>2</sub> composition of PS are extremely low when only 1 mL/h is injected. Furthermore, the promotion effect of 10 mL/h water injection on H<sub>2</sub> yield and composition of PS are also the highest, which increase by 53.91 mmol/g and 21.54 mol% compared to the case when 1 mL/h water injected. This demonstrates the importance and necessity of enough gasification agent for PS to improve the reforming reactions for H<sub>2</sub> production when considering the complicated structure of PS.



Water Injection Flowrate (ml/h)

### Figure 12 Gas composition and yield when changing water injection flowrate

(For all cases under catalyst Ni-CaO-C, Biomass: Plastic = 5:5, Pyrolysis T: 800 °C, Reforming T: 700 °C)

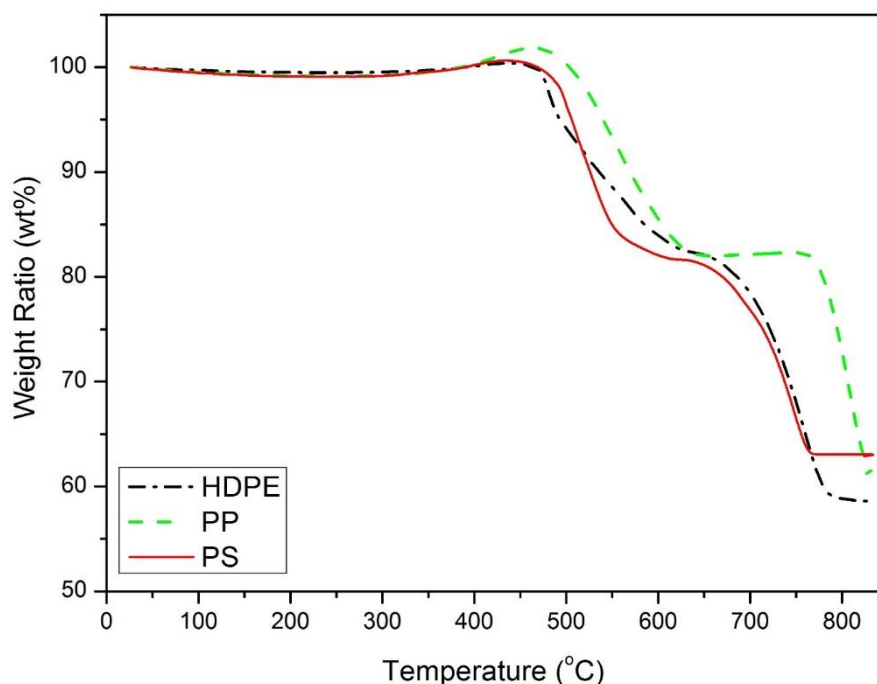
#### 5.4 Summary

Although introduction of plastics as feedstock could promote H<sub>2</sub> production to some extent, excessive plastics in feedstock may hinder release of radicals from biomass and further reactions in reforming stage, thus reducing total gas yield and H<sub>2</sub> yield. In this study, the ideal feedstock ratio is suggest to be biomass : plastics = 7:3. That means the specific plastic content in feedstock mixture could be controlled less than 30 wt%. It should be noted that less than 30 wt% plastics is not definite for all kinds of plastics because experiments are not enough to determine accurate plastic limits in feedstocks mixture in this study. For different combination of plastics and biomass, this limit might be different. However, the phenomena that excessive plastics restricting H<sub>2</sub> yield can be demonstrated.

Among three plastics, HDPE can achieve very high H<sub>2</sub> yield under relatively low reforming temperature at 700 °C and water injection flowrate at 5 mL/h (H<sub>2</sub> yield :80.36 mmol/g). However, under the same conditions, PP and PS only have H<sub>2</sub> yields at 59.35 mmol/g and 38.51 mmol/g. Especially for PS, it requires even higher operating conditions (800°C and 10 mL/h) to ensure acceptable H<sub>2</sub> production. Therefore, pyrolysis/gasification of PS and biomass may consume more energy compared to that of HDPE and PP.

#### 6. Characterisation of used catalyst

TG analysis was carried out on used catalyst Ni-CaO-C to detect the coke formation after experiment. Used catalyst from Exp(10) – (12) in Table 5, *section 4.2* were selected. The results of TG analysis are shown in Figure 13.



**Figure 13 TGA of used catalyst**

**(For all 3 cases under catalyst Ni-CaO-C, Biomass: Plastic = 5:5, Pyrolysis T: 800 °C, Reforming T: 700 °C, Water injection flowrate 5 mL/h)**

Slight weight loss can be observed for all the three used catalysts before 300 °C, which might be due to the evaporation of moisture content. Slight weight increase take place at around 450 °C and the catalyst weight ratio even exceed 100 wt%. This is because that Ni content in catalyst is oxidised into NiO, which increases the catalyst weight (Wu et al., 2013). Then, obvious weight loss stages can be observed for used catalysts used in pyrolysis/gasification of HDPE and PS after 450 °C and another obvious weight loss stages can be observed at around 650 °C. These two stages are combustion of amorphous carbon and filamentous carbon respectively (Wu et al., 2013). Compared to HDPE and PS, PP has higher combustion temperatures of amorphous carbon and filamentous carbon at 500 °C and 750 °C. This demonstrates that the coke deposited on catalyst Ni-CaO-C used in pyrolysis/gasification of PP and biomass is more difficult to be removed compared to that of HDPE and PS.

Because deposited coke and catalyst support (i.e. activated carbon) were combusted together during TGA, it is hard to identify the coke deposit ratio directly from Figure 13. To solve this

problem, the specific coke deposit ratio was calculated using the weight loss ratio of used catalyst to take away the weight loss of fresh catalyst. The coke deposit ratio of three used catalysts are 4.90 wt% (HDPE), 3.11 wt% (PP) and 1.41 wt% (PS). However, it should be noted that the current calculation method of coke deposit ratio is still not very accurate because it does not consider the weight loss of  $\text{CaCO}_3$  decomposition in used catalyst. Therefore, these results are just for general comparison. Among three plastics with biomass, HDPE has the highest deposited coke on catalyst and PS has the lowest deposited coke on catalyst. The reason might be that under the same operating conditions, catalyst Ni-CaO-C has higher catalytic activity to catalyse HDPE with biomass than that of PS. For HDPE, high reaction rate results in high reaction extent, so that it offers necessary conditions as premise for coke formation. For PS, reaction rates as well as reaction extent are restricted in relatively low level, which also restricts possibility to form coke. To summarise, the coke deposit ratio of used Ni-CaO-C catalyst when treating different plastics and biomass are acceptable, which are all lower than 5 wt%.

## **7. Conclusions**

In this paper, co-pyrolysis/gasification of biomass (e.g. pine sawdust) and different plastics (e.g. HDPE, PP and PS) were carried out for  $\text{H}_2$  production under newly developed dual-support catalyst Ni-CaO-C. Characterisation of plastics through TG-FTIR analysis were performed. Among three plastics, alkane is the main product of HDPE. Alkane and methyl are main products of PP. Alkene and benzene derivatives are the main products of PS. The results of plasticss characterisation are used to explain further experiment results. Experimental studies of pyrolysis/gasification of biomass and different plastics without catalyst and with catalyst were compared. The experimental results indicate that the  $\text{H}_2$  yield and composition with catalysts are much higher than those without catalyst for all three plastics, which demonstrates the necessity of catalyst to improve  $\text{H}_2$  production. The  $\text{H}_2$  yield (HDPE: 80.36

mmol/g, PP: 59.35 mmol/g, PS: 38.51 mmol/g) and composition (HDPE: 69.86 mol%, PP: 69.21 mol%, PS: 66.09 mol%) under new catalyst Ni-CaO-C are all observed to be obviously higher than that under traditional catalyst Ni-Al<sub>2</sub>O<sub>3</sub> for three plastics. Therefore, the high performance of catalyst Ni-CaO-C can be demonstrated. The specific catalytic effect of catalyst Ni-CaO-C on H<sub>2</sub> production ranks in the sequence of HDPE>PP>PS. Experimental studies changing operating conditions (feedstock ratio, reforming temperature and water injection flowrate) for biomass and different plastics were also performed. The results indicate that plastic content in feedstock is suggested to be less than 30 wt% ~ 40 wt% (30 wt% for PS; 40 wt% for HDPE and PP), otherwise excessive plastics could restrict H<sub>2</sub> production. Compared to HDPE and PP, PS requires higher reforming temperature and water injection flowrate to ensure acceptable H<sub>2</sub> production, which is more energy consumable. Eventually, characterisation of used catalyst through TG analysis indicates that the coke formation extent for the new catalyst Ni-CaO-C is low when catalysing three plastics with biomass. The specific coke deposit ratio for three plastics are all less than 5 wt%. The new findings in this study will contribute to large scale commercialisation of pyrolysis/gasification technology for H<sub>2</sub> production.

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## References

- Abbas, S.Z., Dupont, V., Mahmud, T. (2017), Kinetics study and modelling of steam methane reforming process over a NiO/Al<sub>2</sub>O<sub>3</sub> catalyst in an adiabatic packed bed reactor, *International Journal of Hydrogen Energy*, 42(5), pp. 2889 – 2903.
- Abdelouahed, L., Authier, O., Mauviel, G., Corriou, J.P., Verdier, G., Dufour, A. (2012), Detailed modeling of biomass gasification in dual fluidized bed reactors under Aspen Plus, *Energy & Fuels*, 26, pp.3840 – 3855.
- Acharya, B., Dutta, A., Basu, P. (2010), An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO, *International Journal of Hydrogen Energy*, 35, pp.1582-1589.
- Alnarabiji, M.S., Tantawi, O., Ramli, A., Asmawati, N., Zabidi, M., Ghanem, O.B., Abdullah, B. (2019), Comprehensive review of structured binary Ni-NiO catalyst: Synthesis, characterization and applications, *Renewable and sustainable energy reviews*, 114, 109326.
- Alvarez, J., Kumagai, S., Wu, C.F., Yoshioka, T., Bilbao, J., Olazar, M., Williams, P.T. (2014), Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification, *International Journal of Hydrogen Energy*, 39, pp. 10883-10891.
- Block, C., Ephraim, A., Hortala, E.W., Minh, D.P., Nzihou, A., Vandecasteele, C. (2018), Co-pyrogasification of plastic and biomass, a review, *Waste and Biomass Valorization*, 10(3), pp.483-509.
- Brachi, P., Chirone, R., Miccio, F., Picarelli, A., Ruoppolo, G. (2014), Fluidized bed co-gasification of biomass and polymeric wastes for a flexible end-use of the syngas: focus on bio-methanol, *Fuel*, 128, pp.88-98.
- Burra, K.G., Gupta, A.K. (2018), Synergistic effects in steam gasification of combined biomass and plastic waste mixtures, *Applied Energy*, 211, pp. 230 – 236.

CaO, C.Q., Bian, C., Wang, G.Y., Bai.B., Xie, Y.P., Jin, H. (2020), Co-gasification of plastics wastes and soda lignin in supercritical water, *Chemical engineering journal*, 388, 124277.

Chai, Y., Gao, N.B., Wang, M.H., Wu, C.F. (2020), H<sub>2</sub> production from co-pyrolysis/gasification of waste plastics and biomass under novel catalyst Ni-CaO-C, *Chemical Engineering Journal*, 382, 122947.

Cho, M.H., Choi, Y.K., Kim, J.S. (2015), Air gasification of PVC (polyvinyl chloride)-containing plastic waste in a two-stage gasifier using Ca-based additives and Ni-loaded activated carbon for the production of clean and hydrogen-rich producer gas, *Energy*, 87, pp.586-593.

Claude, V., Courson, C., Kohler, M., Lambert, S.D. (2016), Overview of essentials of biomass gasification technologies and their catalytic cleaning methods, *Energy & fuels*, 30, pp. 8791-8814.

Erkiaga, A., Lopez, G., Amutio, M., Bilbao, J., Olazar, M. (2014), Influence of operating conditions on the steam gasification of biomass in a conical spouted bed reactor, *Chemical Engineering Journal*, 237, pp. 259-267.

Esfahani, R.A.M., Osmieri, L., Specchia, S., Yusup, S., Tavasoli, A., Zamaniyan, A. (2017), H<sub>2</sub>-rich syngas production through mixed residual biomass and HDPE waste via integrated catalytic gasification and tar cracking plus bio-char upgrading, *Chemical Engineering Journal*, 308, pp. 578-587.

PlasticsEurope (2018), *Plastics – the Facts 2018 An analysis of European plastics production, demand and waste data*.

Gao, N.B., Li, A.M., Quan, C., Du, L., Duan, Y. (2013), TG-FTIR and Py-GC/MS analysis on pyrolysis and combustion of pine sawdust, *Journal of Analytical and Applied Pyrolysis*, 100, pp. 26-32.

- Gao, N.B., Han, Y., Quan, C. (2018), Study on steam reforming of coal tar over Ni-Co/ceramic foam catalyst for hydrogen production: effect of Ni/Co ratio, *International Journal of Hydrogen Energy*, 43, pp. 22170 – 22186.
- Geyer, R., Jambeck, J.R., Law, K.L. (2017), Production, use, and fate of all plastics ever made, *Science Advances*, 3(7), e1700782.
- Hu, G.X., Huang, H. (2009), Hydrogen rich fuel gas production by gasification of wet biomass using a CO<sub>2</sub> sorbent, *Biomass and Energy*, 33, pp.899-906.
- Jacobson, M.Z. (2008), Review of solutions to global warming, air pollution, and energy security, *Energy & Environmental Science*, 2, pp.148-173.
- Kumagai, S., Alvarez, J., Blanco, P.H., Wu, C. F., Yoshioka, T., Olazar, M., Williams, P.T. (2015), Novel Ni-Mg-Al-Ca catalyst for the enhanced hydrogen production for the pyrolysis-gasification of a biomass/plastic mixture, *Journal of Analytical and Applied Pyrolysis*, 113, pp.15-21.
- Kumar, A., Jones, D.D., Hanna, M.A. (2009), Thermochemical Biomass Gasification: A review of the Current Status of the Technology, *Energies*, 2, pp.556-581.
- Kwon, B.W., Oh, H.J., Kim, G.S., Yoon, S.P., Han, J. (2018), The novel perovskite-type Ni-doped Sr<sub>0.92</sub>Y<sub>0.08</sub>TiO<sub>3</sub> catalyst as a reforming biogas (CH<sub>4</sub> + CO<sub>2</sub>) for H<sub>2</sub> production, *Applied Energy*, 227, pp. 213 – 219.
- Law, K.L. (2017), Plastics in the marine environment, *Annual review of marine science*, 9, pp. 205 – 229.
- Li, J.F., Liao, S.Y., Dan, W.Y., J, K.L., Zhou, X.R. (2012), Experimental study on catalytic steam gasification of municipal solid waste for bioenergy production in a combined fixed bed reactor, *Biomass and Bioenergy*, 46, pp.174-180.

- Liu, G.C., Liao, Y.F., Wu, Y.T., Ma, X.Q. (2018), Synthesis gas production from microalgae gasification in the presence of Fe<sub>2</sub>O<sub>3</sub> oxygen carrier and CaO additive, *Applied Energy*, 212, pp. 955 – 965.
- Lopez, G., Erkiaga, A., Amutio, M., Bibao, J., Olazar, M. (2015), Effect of polyethylene co-feeding in the steam gasification of biomass in a conical spouted bed reactor, *Fuel*, 152, pp.393-401.
- Mazumder, J., Lasa, H.I.D (2016), Catalytic steam gasification of biomass surrogates: Thermodynamics and effect of operating conditions, *Chemical Engineering Journal*, 293, pp. 232-242.
- Moldoveanu, S.C. (2019), Pyrolysis of organic molecules: Application to health and environmental issues, 2<sup>nd</sup> Ed. Elsevier, Oxford, UK.
- Møller, K.T., Jensen, T.R., Akiba, E., Li, H.W. (2017), Hydrogen – A sustainable energy carrier, *Progress in Natural Science: Materials International*, 27(1), pp. 34-40.
- Nanou, P., Murillo, H.E.G., Swaaij, W.P.M.V., Rossum, G.V., Kersten, S.R.A. (2013), Intrinsic reactivity of biomass-derived char under gasification conditions-potential of wood ash as catalyst, *Chemical engineering journal*, 217, pp. 289 – 299.
- Pandey, A., Bhaskar, T., Stocker, M., Sukumaran, R.K. (2015), Recent advances in thermochemical conversion of biomass, Elsevier, Oxford, UK.
- Pinto, F., Franco, C., Andre, R.N., Miranda, M., Gulyurtlu, I., Cabrita, I. (2002), Co-gasification study of biomass mixed with plastic wastes, *Fuel*, 81, pp.291-297.
- Pinto, F., Franco, C., Andre, R.N., Tavares, C., Dias, M., Gulyurtlu, I., Cabrita, I. (2003), Effect of experimental conditions on co-gasification of coal, biomass and plastics wastes with air/steam mixtures in a fluidized bed system, *Fuel*, 82, pp.1967-1976.

Ravenni, G., Elhami, O.H., Ahrenfeldt, J., Henriksen, U.B., Neubauer, Y. (2019), Adsorption and decomposition of tar model compounds over the surface of gasification char and active carbon within the temperature range 250 – 800 °C, *Applied energy*, 241, pp.139 – 151.

Ren, J., Cao, J.P., Zhao, X.Y., Wei, F., Liu, T.L., Fan, X., Zhao, Y.P., Wei, X.Y. (2017), Preparation of high-dispersion Ni/C catalyst using modified lignite as carbon precursor for catalytic reforming of biomass volatiles, *Fuel*, 202, pp.345-351.

Saleem, F., Harris, J., Zhang, k., Harvey, A. (2020), Non-thermal plasma as a promising route for the removal of tar from the product gas of biomass gasification – A critical review, *Chemical engineering journal*, 382, 122761.

Sun, Z., Toam, S., Chen, S.Y., Xiang, W.G., Fan, M.H., Zhu, M., Ma, S.W. (2017), Biomass pyrolysis-gasification over Zr promoted CaO-HZSM-5 catalysts for hydrogen and bio-oil co-production with CO<sub>2</sub> capture, *International journal of hydrogen energy*, 42, pp.16031-16044.

Verma, R., Vinoda, K.S., Papireddy, M., Gowda, A.N.S. (2016), Toxic pollutants from plastic waste – A Review, *Procedia Environmental Sciences*, 35, pp. 701-708.

Wu, C.F., Williams, P.T. (2010a), A novel Ni-Mg-Al-CaO catalyst with the dual functions of catalysis and CO<sub>2</sub> sorption for H<sub>2</sub> production from the pyrolysis-gasification of polypropylene, *Fuel*, 89, pp.1435-1441.

Wu, C.F., Williams, P.T. (2010b), Pyrolysis-gasification of post-consumer municipal solid plastic waste for hydrogen production, *International Journal of Hydrogen Energy*, 35, pp.949-957.

Wu, C.F., Wang, Z.C., Dupont, V., Huang, J., Williams, P.T. (2013), Nickel-catalysed pyrolysis/gasification of biomass components, *Journal of Analytical and Applied Pyrolysis*, 99, pp.143-148.

Xu, D., Xiong, Y.Q., Ye, J.D., Su, Y.H., Dong, Q., Zhang, S.P. (2019), Performances of syngas production and deposited coke regulation during co-gasification of biomass and

plastics wastes over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst: Role of biomass to plastic ratio in feedstock,

*Chemical engineering journal*, <https://doi.org/10.1016/j.cej.2019.123728>.

Yan, J.C., Sun, R., Shen, L.H., Bai, H.C., Jiang, S.X., Xiao, Y. (2020), Hydrogen-rich syngas production with tar elimination via biomass chemical looping gasification (BCLG) using BaFe<sub>2</sub>O<sub>4</sub> / Al<sub>2</sub>O<sub>3</sub> as oxygen carrier, *Chemical engineering journal*, 387, 1241107.

Yao, D.D., Hu, Q., Wang, D.Q., Yang, H.P., Wu, C.F., Wang, X.H., Chen, H.P. (2016), Hydrogen production from biomass gasification using biochar as a catalyst/support, *Bioresource technology*, 216, pp.159-164.

Zhou, H., Nebg, A.H., Long, Y.Q., Li, Q.H., Zhang, Y.G. (2014), Classification and comparison of municipal solid waste based on thermochemical characteristics, *Journal of the Air & Waste Management Association*, 64(5), pp.597-616.

Zhang, X.S., Lei, H.W., Chen, S.L., Wu, J. (2016), Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review, *Green chemistry*, 18, pp. 4145 – 4169.