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Catalytic dry reforming of waste plastics from different waste treatment plants for production of synthesis gases

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Abstract:

Catalytic dry reforming of mixed waste plastics, from a range of different municipal, commercial and industrial sources, were processed in a two-stage fixed bed reactor. Pyrolysis of the plastics took place in the first stage and dry (CO_2) reforming of the evolved pyrolysis gases took place in the second stage in the presence of Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts in order to improve the production of syngas from the dry reforming process. The results showed that the highest amount of syngas yield was obtained from the dry reforming of plastic waste from the agricultural industry with the Ni/Al_2O_3 catalyst, producing 153.67 $mmol_{syngas}\ g^{-1}{}_{waste}$. The addition of cobalt metal as a promoter to the Ni/Al_2O_3 catalyst did not have a major influence on syngas yield. Overall, the catalytic-dry reforming of waste plastics from various waste treatment plants showed great potential towards the production of synthesis gases.

Keywords: Waste; Plastics; Reforming; Carbon dioxide; Catalyst

1. Introduction

Waste management is a critical issue in many countries with an ever increasing impact on the environment. The plastic fraction of waste represents a considerable proportion of the total waste stream. The world production of plastics is reported to be ~300 million tonnes/year and produces products for a wide range of applications. The dominant plastics produced worldwide are polyethylene (29.6%), polypropylene (18.9 %), polyvinyl chloride (10.4%), polystyrene (7.1%), polyethylene terephthalate (6.9%), polyurethane (7.4%) and many other types of plastic which represent about 19.7% of the plastics produced (PlasticsEurope, 2015). Depending on the end-use of the plastic product, at some stage during the lifetime of the plastic, the plastic will end up as waste in various, commercial, industrial and household waste sectors (Shonfield, 2008). Waste plastics may be separated from the various waste streams for subsequent recycling, recovery and re-processing. The vast majority of plastic recycling is through mechanical recycling. However, alternative methods for producing fuels and petrochemical feedstocks from waste plastics are being investigated (Shonfield, 2008).

One such process is dry reforming, where carbon dioxide is used instead of steam for the catalytic reforming of hydrocarbons for the production of syngas. Dry reforming processes involve cracking of the high molecular weight feedstock hydrocarbons with carbon dioxide to produce synthesis gases (syngas - hydrogen and carbon monoxide). Current research is more focused on the dry reforming of methane, ethanol and glycerol (Al-Doghachi et al, 2015; Hou et al., 2015; Siew et al., 2015; Ayodele et al., 2016; Matei-Rutkovska et al., 2016). However, waste plastics represent a feedstock which has a high content of carbon and hydrogen which may be suitable as an alternative source for the process (Deanin, 1987). Therefore, the dry reforming of waste plastics could be a potential treatment process for the production of syngas. The waste plastics may be pyrolysed to produce a suite of hydrocarbon gases which are passed directly to a second stage reactor where dry reforming takes place in the presence of the carbon dioxide and a catalyst (Saad et al., 2015a; Saad et al, 2015b). A further point in support of the dry reforming process is the current interest in finding viable uses for the large amounts of carbon dioxide which are predicted to be available in the future through carbon dioxide capture and storage processes. The prediction of the expansion of such carbon capture processes are expected to mitigate against climate change.

To improve the dry reforming process, there has been research into the development of catalysts to enhance the production of syngas. Recent reviews on the use of catalysts in the dry reforming process suggest that Ni-based catalysts are the most suitable option due to their low cost and relatively high catalytic activity (Zagaynov et al., 2016; Theofanidis et al., 2016). Studies have reported that the addition of a metal promoter to Ni-based catalysts can further improve the production of syngas from the dry reforming process by improving the structure and uniformity of the catalyst particles resulting in better metal dispersion. For example, the addition of Pt, Co, Mg, or Cu (Foo et al., 2012; Sun et al., 2012; Mahoney et al., 2014; Sharifi et al, 2014; Wu et al., 2015) as metal promoters have been reported to produce catalysts which inhibit carbon deposition and show high catalytic activity towards syngas production from the dry reforming of methane. However, it is uncertain whether such metal promoted catalysts would be effective for the dry reforming of the wide range of hydrocarbons derived from the pyrolysis of waste plastics.

In this paper, waste plastics derived from a range of different municipal, commercial and industrial sources have been subject to the catalytic dry reforming process with the aim of maximising the production of syngas. The plastic waste samples included; mixed plastics from household waste packaging; mixed plastics from a building construction site; mixed plastics from agriculture; mixed plastics from electrical and electronic equipment (refrigerator and freezer, old style television sets and monitors); refuse derive fuel containing waste plastics and other waste materials and a simulated mixture of municipal solid waste plastic. The catalysts used were Ni/Al_2O_3 and $Ni-Co/Al_2O_3$ which were prepared by the rising-PH technique (Garcia et al., 2002).

2. Materials and Methods

2.1 Raw materials.

A range of real-world waste plastic containing samples were obtained from different sources. The mixed plastic from household packaging waste (MP_{HP}) was collected and recycled from Fost Plus in Belgium and mainly consisted of HDPE and PET. The 5.0 mm sized flakes of MP_{HP} were obtained from a low density fraction through the air separation process. In addition, mixed plastics from building construction waste (MP_{BC}) and mixed plastics from waste agriculture waste (MP_{AGR}) were obtained from University of Pannonia, Hungary. The agricultural waste plastics (MP_{AGR}) consisted of high/low density polyethylene and polypropylene, while mixed plastic waste from building construction (MP_{BC}) contained mainly polystyrene, polyurethane, polyethylene and polypropylene. Mixed plastics from waste electrical and electronic equipment were recycled from a commercial waste treatment plant that specifically recovered the plastics from this type of waste. Three different type of plastic waste were collected from this treatment plant; plastics from waste refrigerator and freezer equipment (MP_F), mixed plastics recovered from old style cathode ray tube television sets and computer monitors (MP_{CRT}) and a plastic mixture from a range of waste electrical and electronic equipment (MP_{WEEE}). Refuse derived fuel (RDF) was also investigated representing processed municipal solid waste with metals and glass removed and was mainly composed of plastics, paper, board, wood and textile materials. In addition, a mixture of low density and high density polyethylene (LDPE, HDPE) polystyrene (PS), polyethylene terephthalate (PET) and polypropylene (PP) was also examined to simulate the plastic wastes found in municipal solid waste (SWP). The composition was based on the report by Delgado et al. (2007) and consisted of; 42 wt.% of LDPE, 20 wt.% of HDPE, 16wt.% of PS, 12 wt.% of PET and 10wt.% of PP. All of the plastic waste samples were prepared to approximately the sample particle size of between 2 mm – 10 mm. The analysis data for each waste are summarized in Table 1.

2.2 Preparation of catalyst

Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts were prepared using the rising-pH technique (Garcia et al., 2002). 200 ml deionised water was used to mix the solution containing $Ni(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ either with or without $Co(NO_3)_2.6H_2O$. The aqueous solution was stirred moderately at 40 °C. The precipitant of 1 M ammonium solution was added until the pH value of 8.3 was reached. The precipitates were filtered, dried overnight and calcined. The catalysts were crushed and sieved at a particle size of 50 – 212 μm. The addition of cobalt metal to the Ni/Al_2O_3 catalyst was chosen based on its performance in our previous study into the dry reforming of high density polyethylene; showing high catalytic activity towards syngas production (Saad et al., 2015b).

2.3 Two-stage fixed bed reactor system

A two-stage fixed bed reactor system was used in this study as discussed in our previous work (Saad et al., 2015b). The pyrolysis of the waste plastic sample took place in the first stage reactor while the catalytic dry reforming of the derived pyrolysis gases took place in the second stage reactor. The reactors were heated by two separate electrical furnaces which were separately temperature controlled and monitored. The experimental procedure consisted of preheating the second reactor to 800 °C and where 1 g of catalyst was placed. The first stage pyrolysis reactor contained 2 g of plastic sample held in a sample holder and was heated to 500 °C with a heating rate of 10 °C min^{-1} and held at that temperature for 30 minutes. The reforming gas, CO_2, was injected into the second catalytic reactor and N_2 was used as a carrier gas with a flow rate of 50.9 ml min^{-1} (6 g h^{-1}) and 200 ml min^{-1} respectively.

The product gases were cooled using a three-stage condenser system, one condenser at ambient temperature and two condensers cooled with dry ice which served to trap any condensable liquid. The uncondensed gaseous products were collected in a Tedlar™ sample gas bag for off-line analysis using two Varian 3380 Gas Chromatography (GC) analysers as described previously (Saad et al., 2015a; Saad et al., 2015b). The gas results reported represents the total gas produced during the process and trapped in the Tedlar gas sample bag. The mass of gases produced was obtained from the known flow rates and molecular mass of the individual gases, rather than mass by difference

CO_2 conversion was determined as gram per gram of waste plastic input by deducting the amount of CO_2 in the sample gas bag from the total amount of CO_2 introduced into the system. It should be noted that due to the nature of the waste plastic samples used, some of which contain oxygen, CO_2 might also be produced during the pyrolysis/reforming process from the waste plastics.

2.4 Carbon deposition characterization

The characterization of carbon deposited on the catalyst surface during the experimental procedure was performed using temperature programmed oxidation (TPO) and scanning electron microscopy (SEM). TPO experiments were conducted using a thermogravimetric analyser (TGA-50 Shimadzu). The procedure was to heat ~10 mg of the reacted catalyst from ambient temperature to 800 °C at 15 °C min^{-1} under an air atmosphere. In addition, the nature of the carbon morphologies deposited on the catalyst surface were also analysed using a Hitachi SU8230 high resolution SEM analyser.

3. Results and discussion

3.1 Product yield.

The product yields from the catalytic-dry reforming of the different type of plastic wastes with Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalyst are shown in Figure 1. Mass closures of between 97 – 103 wt.% were found from the experiments which was deemed as acceptable. Mass closure higher than 100 wt.% were probably due to experimental errors, errors in weighing or errors in mass flow fluctuations etc.

Figure 1 shows that more than 80 % of the product yield distribution from the dry reforming process with the Ni/Al_2O_3 catalyst were gases. The agricultural plastic waste, MP_{AGR}, showed the highest amount of gas produced with 100.28 wt.% followed by the household plastic packaging waste, MP_{HP} with a gas yield of 99.86 wt.%. The simulated waste plastics, SWP produced 98.21 wt.% gas and the building construction plastic waste MP_{BC} produced 97.51 wt.% gas. The other waste plastic samples produced between 85.6-91.8 wt% gas yield. Based on the proximate analysis data shown in Table 1, the plastic mixture wastes (MP_{HP}, MP_{BC}, MP_{AGR}) were high in volatile content, at more than 97 %, followed by plastics from WEEE (MP_{CRT}, MP_F and MP_{WEEE}). RDF contained the lowest volatile content, hence producing the lowest gas yield from the catalytic-dry reforming process. In comparison, RDF showed the highest yield of liquid with 4.20 wt.% whereas MP_F only produced 0.80 wt.%. Char yield from RDF sample was also the highest at 6.70 wt.%. The carbon deposited on the Ni/Al_2O_3 catalyst from the dry reforming of MP_{CRT} showed the highest carbon deposition with 6.30 wt.%.

The addition of Co metal in the Ni/Al_2O_3 based catalyst ($Ni\text{-}Co/Al_2O_3$) appeared to reduce the production of gases, with the reduction range from the smallest of 0.4 % decrease for MP_{CRT} to 88.47 wt.%, to the largest of decrease of 8.6 % for MP_{AGR} reducing the gas yield to 91.63 wt.%. However, the amount of liquid yield was increased for MP_{BC}, MP_{AGR}, MP_F, MP_{CRT} and RDF but reduced for MP_{HP}, MP_{WEEE} and SWP. A similar trend of the highest char and carbon deposition yields were found in the experiment with $Ni\text{-}Co/Al_2O_3$ catalyst; RDF with 6.50 wt.% and MP_{CRT} with 5.10 wt.% respectively, although the amount were lower compared to the carbon deposition with the Ni/Al_2O_3 catalyst.

3.2 Gas composition and syngas production from dry reforming of waste plastics.

The gas compositions; carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and C_2-C_4 hydrocarbons for each type of plastic waste from the catalytic-dry reforming process of the different types of waste samples with the influence of Ni/Al_2O_3 catalyst and Ni-Co/Al_2O_3 catalyst are shown in Table 2 and Table 3 respectively. For both the Ni/Al_2O_3 and Ni-Co/Al_2O_3 catalysts, the main gases produced from the catalytic-dry reforming process were carbon monoxide and smaller concentrations of hydrogen, methane and C_2-C_4 hydrocarbons, suggesting that the reformation of gaseous product with CO_2 occurred in the 2nd reactor mainly via the dry reforming reaction (Equation 1).

$$CxHy + xCO_2 \rightarrow 2xCO + y/2\ H_2 \qquad \text{Equation 1}$$

Dry reforming with the Ni/Al_2O_3 catalyst with MP_{HP}, MP_{BC}, MP_{AGR} and SWP produced the highest CO and H_2 production with a close range of between 2.7 to 2.9 $g_{gas}\ g^{-1}_{waste}$ for CO and 0.09 to 0.1 $g_{gas}\ g^{-1}_{waste}$ for H_2. These four waste plastics contained high amounts of hydrogen and carbon as shown in Table 1. The RDF sample produced the lowest amount of CO and H_2 concentration with only 0.9 and 0.02 $g_{gas}\ g^{-1}_{waste}$ respectively, caused by the high oxygen content of the waste sample as shown in Table 1, at ~50 wt.%. It is shown that from the data in Table 2, high CO_2 conversion resulted in high syngas yield and low CO_2 conversion resulted on low syngas yield. The syngas yield and CO_2 conversion for catalytic-dry reforming of the different types of plastic wastes with the influence of Ni/Al_2O_3 catalyst were in the following order: MP_{AGR} > MP_{HP} > MP_{BC} > SWP > MP_{WEEE} > MP_{CRT} > MP_F > RDF.

The influence of Co metal addition into the Ni/Al_2O_3 based catalysts produced different gas compositions for each type of waste compared to the Ni/Al_2O_3 catalyst. However, the yield of CO still dominated the gas yields from the catalytic-dry reforming process. In addition, the relationship between syngas yield and CO_2 conversion remained the same for the Ni-Co/Al_2O_3 catalyst, in which high CO_2 conversion resulted on high yield of syngas production. The dry reforming process over the Ni-Co/Al_2O_3 catalyst showed an improvement in syngas yield except for the waste plastic samples, MP_{BC}, MP_{AGR} and MP_F. It is suggested that the addition of cobalt metal promotes either the reduction of heavy hydrocarbon liquid yield through the formation of light hydrocarbon gases (MP_{HP}, MP_{WEEE}, SWP and RDF) or reduction of carbon due to carbon gasification (MP_{CRT} and RDF). The syngas yield and CO_2 conversion for catalytic-dry reforming of the difference types of plastic wastes with the Ni-Co/Al_2O_3 catalyst were in the order: MP_{HP} > SWP > MP_{BC} > MP_{AGR} > MP_{CRT} > MP_{WEEE} > MP_F > RDF.

Sidik et al. (2016) for the dry reforming of methane, reported that the addition of cobalt metal over Ni/MSN (mesoporous silica nanoparticle) catalyst introduced more active sites by improving the Ni dispersion and Ni particle size, therefore, increasing the CH_4 conversion. However, the behaviour of the Ni-Co catalyst toward syngas production may vary based on the feedstock introduced. The optimization of catalyst performance may be implemented to improve the syngas production for example, by varying the calcination temperature, metal loading and preparation method (Goicoechea et al., 2016; Ramasamy, 2015).

Overall, in relation to syngas production from the dry reforming of the various plastic wastes over Ni/Al_2O_3 and Ni-Co/Al_2O_3 catalysts can be summarized as follows; a high yield of syngas is produced from (MP_{HP}, MP_{BC}, MP_{AGR} and SWP) followed by mixed plastics from electrical and electronics equipment waste plants (MP_F, MP_{CRT} and MP_{WEEE}) with the lowest yield of syngas produced from RDF. In comparison to the use of steam in the reforming process compared to the work reported here with carbon dioxide, the syngas production from steam reforming of waste plastics shows a high concentration of hydrogen (Ruoppolo et al., 2012; Acomb et al., 2013; Dou et al, 2016). However, with CO_2 dry reforming, more carbon monoxide is obtained due to the promotion of steam reforming reactions that produces more hydrogen than carbon monoxide. It should also be noted that for the further development of the process, steam could be introduced which would convert the product carbon monoxide to hydrogen via the water gas shift reaction.

The results for the simulated mixture of municipal solid waste plastics (SWP) showed a syngas yield of 140.53 $mmol_{syngas}\ g^{-1}{}_{waste}$ and 148.56 $mmol_{syngas}\ g^{-1}{}_{waste}$ for the Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts respectively. These results were similar to the value obtained for the real-world household waste packaging plastic, suggesting that the composition of the SWP was a close approximation to real-world municipal solid waste plastics.

3.3 Coke formation on the catalysts

Temperature programmed oxidation (TPO) experiments were carried out for the reacted Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts from the dry reforming of the various waste plastics. The plotted thermographs of TGA-TPO and DTG-TPO for the reacted catalysts derived from the catalytic dry reforming of MP_{HP}, MP_{BC}, MP_{AGR}, MP_F, MP_{CRT}, MP_{WEEE}, RDF and SWP are shown in Figure 2 and Figure 3 respectively. The TGA-TPO-weight loss thermographs as shown in Figure 2 indicated that the reacted Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts derived from dry reforming of MP_{CRT} and MP_F produced more deposited carbon on the catalyst surface compared to the other types of wastes. From Figure 3, an obvious coke oxidation peak occurred at around a temperature of

650 °C to 700 °C for the reacted Ni/Al_2O_3 catalyst from dry reforming of MP_{CRT} and MP_F compared to other wastes. However, several temperature weight loss peaks related to carbon combustion occurred in the TPO experiments with the reacted Ni-Co/Al_2O_3 catalysts. The first temperature peak range was observed at around 550 - 600 °C (MP_{AGR}, MP_{CRT}, SWP), a second temperature peak range occurred at around 630 - 700 °C (MP_{BC}, MP_{AGR}, MP_F, MP_{CRT} and MP_{WEEE}) and the third temperature peak occurred at around 740 - 760 °C (MP_{HP}, MP_F, MP_{CRT}, SWP, RDF). It is suggested that carbon combustion at high temperature was due to the combustion of the filamentous whisker type carbons formed on the surface of the catalyst, while low temperature carbon oxidation could be assigned to the combustion of the layered carbons which encapsulate the catalyst and which were formed on the catalyst (Wang, 1999). The encapsulating layered type carbons are reported to deactivate the catalyst active metal sites whereas the filamentous type carbons have less of a deactivation effect, since the formed carbons grow away from the catalyst surface (Wu and Williams, 2010).

Figure 4 and Figure 5 present the SEM morphologies of the reacted catalysts obtained from the catalytic-dry reforming of the plastic wastes. The carbon deposits on the Ni/Al_2O_3 and Ni-Co/Al_2O_3 catalyst surface were investigated and show that in Figure 4, noticeable filamentous whisker type carbons can be seen on the Ni/Al_2O_3 catalyst surface for the dry reforming of the MP_{BC}, MP_{AGR}, MP_{CRT} and SWP plastic wastes. Fu et al. (2016) also reported a similar coke formation on the coked Ni/Al_2O_3 catalyst in their studies into the dry reforming of bio-oil model compounds, indicating the formation of graphite carbon and filamentous carbon fibres. On the other hand, for the reacted Ni-Co/Al_2O_3 catalysts as presented in Figure 5, the filamentous whisker type carbons were observed on the catalyst for the MP_{BC}, MP_{AGR} and MP_{CRT} and also for RDF, while the amount was reduced for SWP.

An obvious structural change between the reacted Ni/Al_2O_3 catalyst and Ni-Co/Al_2O_3 catalysts were observed from the catalysts derived from dry reforming of the various waste plastics. Some catalysts showed an increase in the diameter of catalyst particles from the experiment with Ni/Al_2O_3 catalyst to Ni-Co/Al_2O_3 (MP_{BC}, MP_{AGR} and MP_F), a growth of whisker carbons in RDF, some showing a reduction of catalyst diameter (MP_{CRT} and MP_{WEEE}) and some catalysts showing reduction of whisker carbons (MP_{HP} and SWP). Based on the increase of carbon deposition from the dry reforming of MP_{BC}, MP_{AGR} and MP_F with the Ni-Co/Al_2O_3 catalyst compared to the experiments with the Ni/Al_2O_3 catalyst (Figure 1), it can be seen that decreased syngas production was found. This may be attributed to deactivation of the catalyst caused by the formations of carbon on the catalysts, hence blocking the access of the reactant gases into the catalysts (Lee et al., 2014; Vicente et al., 2014).

It should also be noted, that in relation to the TGA-TPO-weight loss thermographs from Figure 2 that more weight gain occurred in the TPO experiment with the reacted Ni-Co/Al_2O_3 catalyst compared to the TPO experiment with the reacted Ni/Al_2O_3 catalyst. The weight gain peak was observed starting at the temperature around 400 °C to 500 °C for both of the reacted Ni-based catalysts which was attributed to the oxidation of nickel particles. The addition of Co metal showed a further increment of the weight gain peak. Tompkins and Augis (1981) reported that the oxidation of metallic Co to CoO and Co_3O_4 occurred at a temperature of 425 °C. This suggests that overlapping weight gain as determined by the TGA-TPO occurred between both nickel and cobalt particles for the reacted Ni-Co/Al_2O_3 catalyst from the dry reforming of various wastes, hence a higher weight gain peak.

4. Conclusions

Catalytic dry reforming of a range of municipal, commercial and industrial waste plastics has proven successful in producing significant amounts of synthesis gases. Plastics collected from household packaging, building construction and agricultural (MP_{HP}, MP_{BC} and MP_{AGR}) showed higher yields of syngas production for both Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts, followed by plastics from electrical and electronic equipment waste plastics (MP_F, MP_{CRT} and MP_{WEEE}). On the other hand, RDF showed the least amount of syngas production and less than 1.0 $g_{co2}\ g^{-1}{}_{waste}$ of CO_2 conversion compared to other plastic samples. The addition of Co metal to the Ni/Al_2O_3 catalyst showed a mixed outcome in relation to syngas production, demonstrating that different types of waste plastics might need different metal promoters to improve the production of syngas. The carbon deposits on the Ni-based catalysts have a different nature of formation depending on the type of waste sample being used.

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Table 1. Compositions of proximate and ultimate analysis for each individual waste.

Type of waste	**N$^{\#}$ (wt.%)**	**C$^{\#}$ (wt.%)**	**H$^{\#}$ (wt.%)**	**O$^{\#}$ (wt.%)**	**S* (wt.%)**	**Ash$^{\#}$ (wt.%)**	**Volatile* (wt.%)**	**Moisture$^{\#}$ (wt.%)**	**Fixed Carbon$^{\#}$ (wt.%)**
Mixed plastics from household packaging/ **MP$_{\mathbf{HP}}$**	0.16	82.90	13.37	3.57	0.23	0.90	99.15	1.74	-
Mixed plastics from building construction/ **MP$_{\mathbf{BC}}$**	0.14	80.91	12.22	6.74	0.22	0.49	99.02	0.81	-
Mixed plastics from agriculture/ **MP$_{\mathbf{AGR}}$**	0.89	79.08	12.91	7.12	0.26	1.26	99.06	0.99	-
Mixed plastics from freezer and refrigerator equipment/ **MP$_{\mathbf{F}}$**	1.15	71.95	6.86	20.05	0.22	20.10	81.99	0.80	-
Mixed plastic from cathode ray tube/ **MP$_{\mathbf{CRT}}$**	4.82	85.10	7.80	2.29	0.26	1.40	93.88	3.71	1.02
Mixed plastics from electrical and electronic equipment/ **MP$_{\mathbf{WEEE}}$**	0.70	75.17	5.87	18.26	0.22	2.89	81.04	0.28	15.79
Refuse derived fuel/ **RDF**	0.58	44.78	6.23	48.41	0.29	11.32	70.74	4.47	13.48
Simulated waste plastics/ **SWP**	0.03	83.17	12.00	5.12	0.22	1.13	97.33	1.00	1.57

*dry basis, $^{\#}$received basis

#SWP based on calculation of each plastic component

Table 2. Gas compositions, syngas yield and CO_2 conversion from dry reforming of waste samples with Ni/Al_2O_3 catalyst at 800 °C temperature.

Waste sample	**MP_{HP}**	**MP_{BC}**	**MP_{AGR}**	**MP_{F}**	**MP_{CRT}**	**MP_{WEEE}**	**RDF**	**SWP**
Gas composition (g_{gas} g^{-1}_{waste})								
CO	2.805	2.693	2.915	1.391	1.497	1.796	0.883	2.67
H_2	0.093	0.096	0.1	0.046	0.053	0.043	0.02	0.091
CH_4	0.08	0.05	0.07	0.02	0.02	0.01	0.01	0.04
C_2-C_4	0.02	0.001	0.011	0.001	0.002	0.0	0.0	0.0
Syngas yield ($mmol_{syngas}$ g^{-1}_{waste})								
$Syngas_{H_2+CO}$	146.32	143.85	153.67	72.51	79.84	85.49	41.24	140.53
CO_2 conversion (inlet-outlet) (g_{co2} g^{-1}_{waste})								
CO_{2conv}	2.00	1.97	2.08	0.88	1.13	1.25	0.63	1.89

Table 3. Gas compositions, syngas yield and CO_2 conversion from dry reforming of waste samples with Ni-Co/Al_2O_3 catalyst at 800 °C temperature.

Waste sample	**MP_{HP}**	**MP_{BC}**	**MP_{AGR}**	**MP_F**	**MP_{CRT}**	**MP_{WEEE}**	**RDF**	**SWP**
Gas composition (g_{gas} g^{-1}_{waste}								
CO	2.958	2.696	2.222	1.425	1.784	1.784	0.873	2.79
H_2	0.102	0.091	0.085	0.043	0.058	0.047	0.021	0.099
CH_4	0.081	0.04	0.096	0.014	0.006	0.004	0.017	0.035
$C_2 – C_4$	0.01	0.0	0.027	0.0	0.0	0.0	0.0	0.0
Syngas yield ($mmol_{syngas}$ g^{-1}_{waste})								
$Syngas_{H2+CO}$	156.45	141.47	121.26	72.12	92.63	87.26	41.49	148.56
CO_2 conversion (inlet-outlet) (g_{co2} g^{-1}_{waste})								
CO_{2conv}	2.22	1.95	1.85	1.16	1.42	1.28	0.78	2.07

Figure Captions

Figure 1. Product yields from catalytic-dry reforming of different waste samples with Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts.

Figure 2. TGA-TPO weight loss thermographs of coked Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts after dry reforming of different type of waste samples.

Figure 3. DTG-TPO thermographs of coked Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts after dry reforming of different type of waste samples.

Figure 4. SEM morphologies of coked Ni/Al_2O_3 catalysts after dry reforming of different type of waste samples.

Figure 5. SEM morphologies of coked $Ni\text{-}Co/Al_2O_3$ catalysts after dry reforming of different type of waste samples.

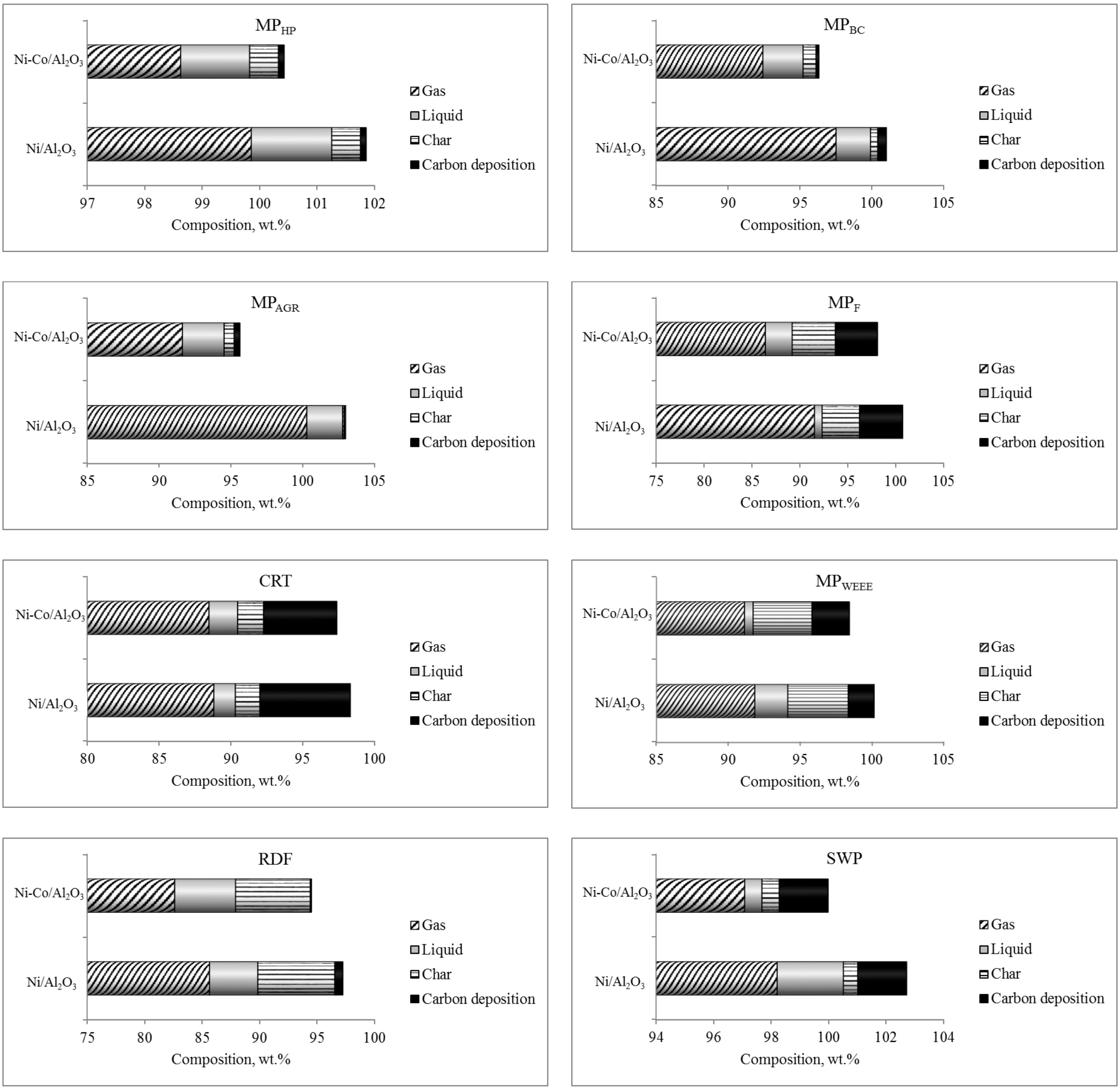
MP_HP
Ni-Co/Al2O3
Ni/Al2O3
97
98
99
100
101
102
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
MP_BC
Ni-Co/Al2O3
Ni/Al2O3
85
90
95
100
105
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
MP_AGR
Ni-Co/Al2O3
Ni/Al2O3
85
90
95
100
105
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
MP_F
Ni-Co/Al2O3
Ni/Al2O3
75
80
85
90
95
100
105
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
CRT
Ni-Co/Al2O3
Ni/Al2O3
80
85
90
95
100
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
MP_WEEE
Ni-Co/Al2O3
Ni/Al2O3
85
90
95
100
105
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
RDF
Ni-Co/Al2O3
Ni/Al2O3
75
80
85
90
95
100
Composition, wt.%
Gas
Liquid
Char
Carbon deposition
SWP
Ni-Co/Al2O3
Ni/Al2O3
94
96
98
100
102
104
Composition, wt.%
Gas
Liquid
Char
Carbon deposition

Figure 1

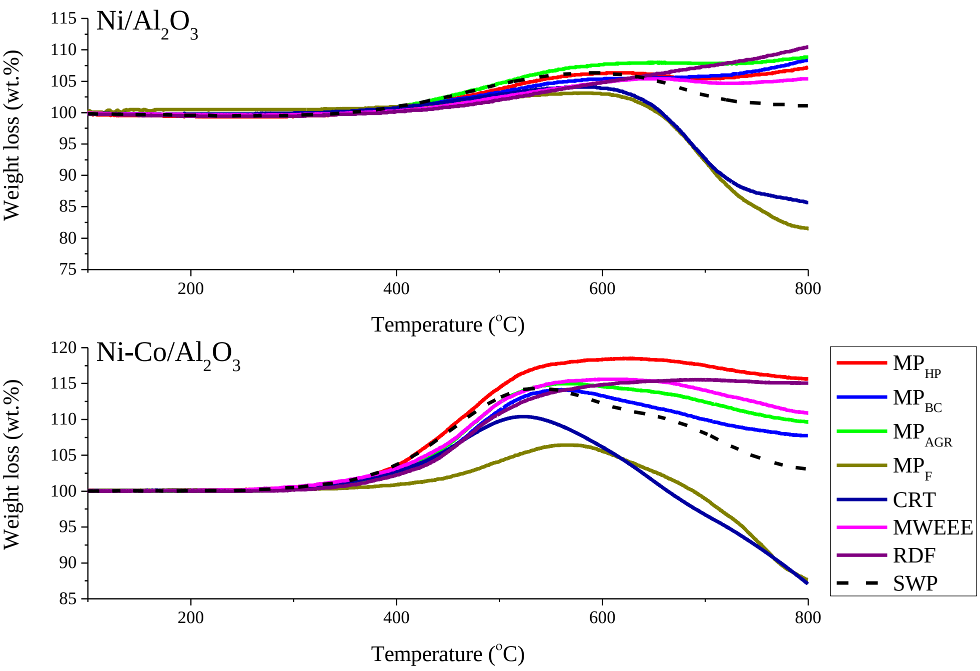
Ni/Al$_2$O$_3$
Weight loss (wt.%)
115
110
105
100
95
90
85
80
75
200
400
600
800
Temperature (°C)
Ni-Co/Al$_2$O$_3$
Weight loss (wt.%)
120
115
110
105
100
95
90
85
200
400
600
800
Temperature (°C)
MP$_{HP}$
MP$_{BC}$
MP$_{AGR}$
MP$_F$
CRT
MWEEE
RDF
SWP

Figure 2

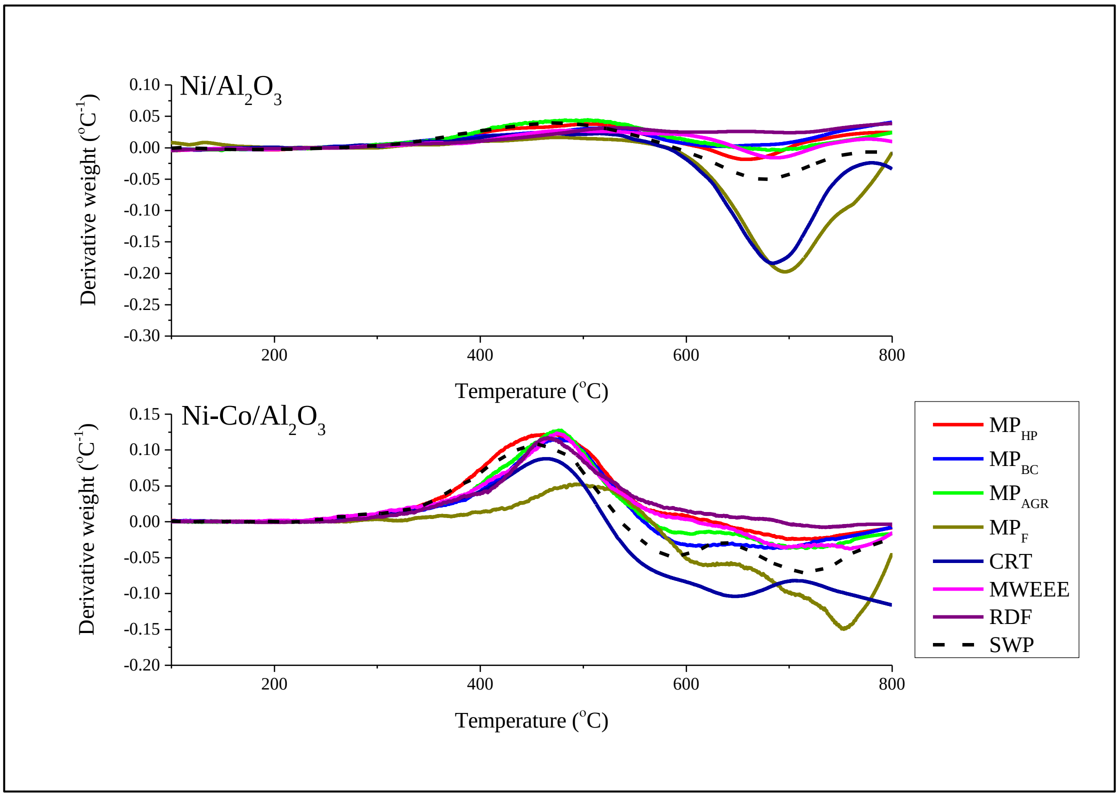
Ni/Al$_2$O$_3$
Derivative weight (°C^{-1})
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
200
400
600
800
Temperature (°C)
Ni-Co/Al$_2$O$_3$
Derivative weight (°C^{-1})
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
200
400
600
800
Temperature (°C)
MP$_{HP}$
MP$_{BC}$
MP$_{AGR}$
MP$_F$
CRT
MWEEE
RDF
SWP

Figure 3

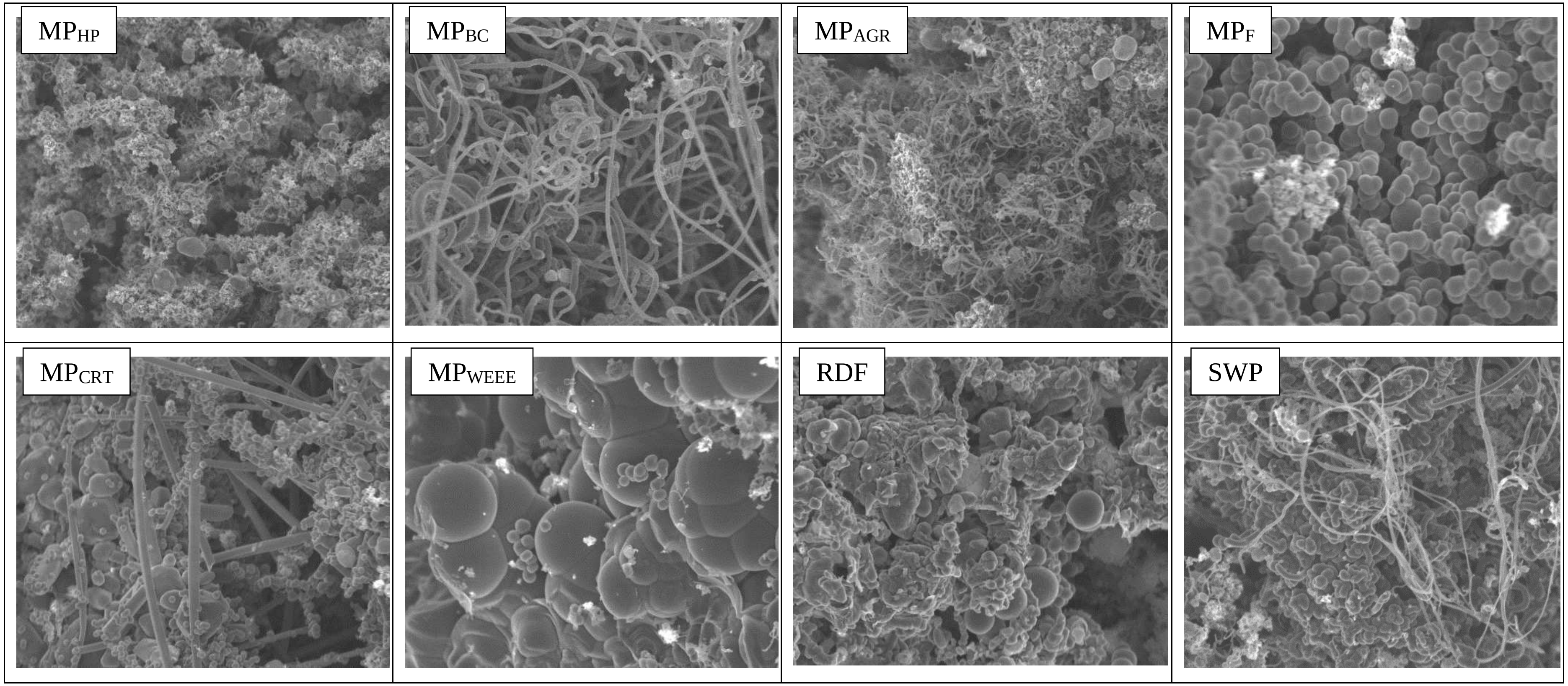

Figure 4

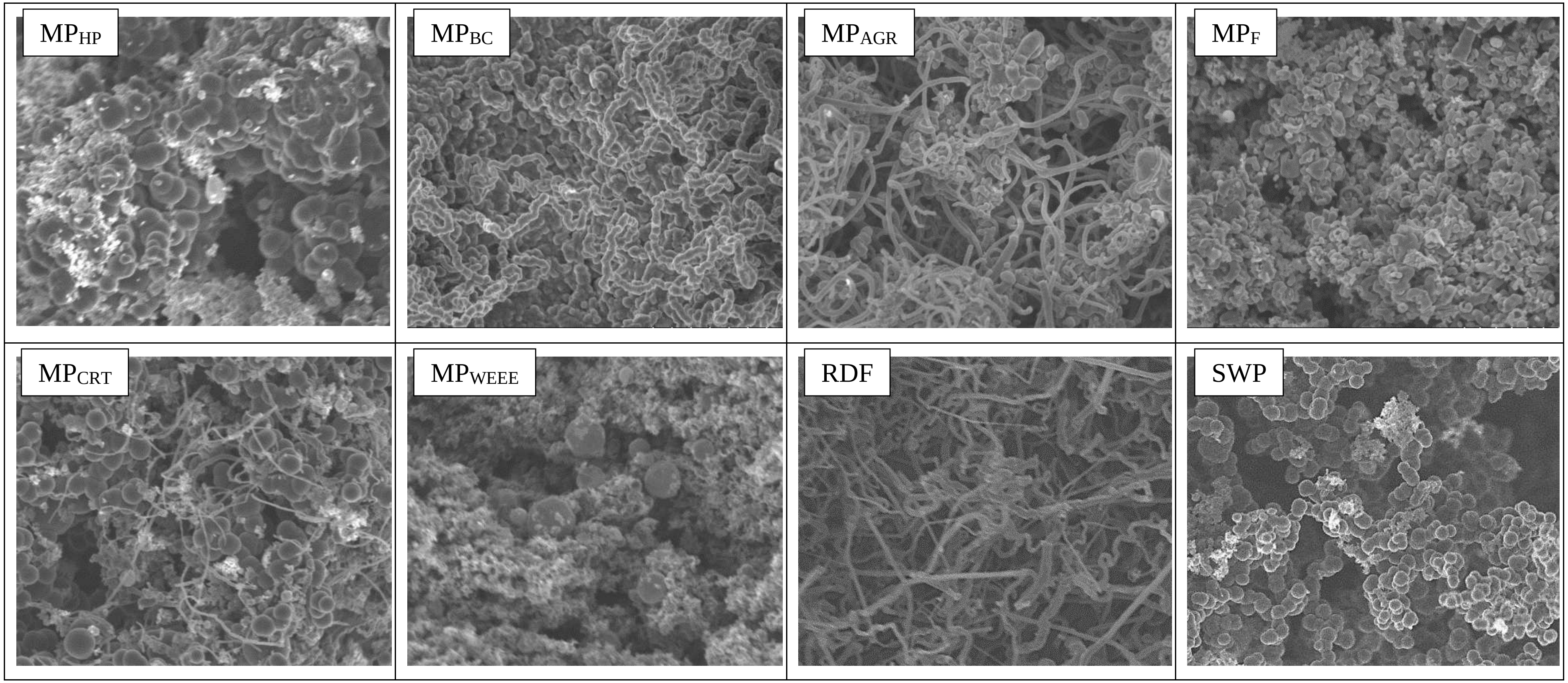

Figure 5