



UNIVERSITY OF LEEDS

This is a repository copy of *Manipulating the H₂/CO ratio from dry reforming of simulated mixed waste plastics by the addition of steam*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/108280/>

Version: Accepted Version

Article:

Saad, JM and Williams, PT (2017) Manipulating the H₂/CO ratio from dry reforming of simulated mixed waste plastics by the addition of steam. *Fuel Processing Technology*, 156. pp. 331-338. ISSN 0378-3820

<https://doi.org/10.1016/j.fuproc.2016.09.016>

© 2016 Elsevier B.V. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International
<http://creativecommons.org/licenses/by-nc-nd/4.0/>

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

1 **Manipulating the H₂/CO Ratio from Dry Reforming of Simulated Mixed Waste**
2 **Plastics by the Addition of Steam**

3 Juniza Md Saad, Paul T. Williams*

4
5 School of Chemical and Process Engineering
6 The University of Leeds, Leeds, LS2 9JT, UK
7 (*Tel: #44 1133432504; Email: p.t.williams@leeds.ac.uk)

8 **ABSTRACT**

9 Two-stage pyrolysis-catalytic reforming of plastics was investigated with the aim of
10 producing usable quality synthesis gases (syngas) comprised of H₂ and CO. The process
11 consisted of pyrolysis of the plastics in the first stage and catalytic reforming with CO₂
12 and steam as the reforming agents in the second stage. The plastics used were a mixture
13 of waste plastics prepared to represent those found in municipal solid waste and the
14 catalysts studied were Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ prepared by the rising pH
15 technique. A range of different CO₂/steam ratios were considered; 4:0, 4:0.5, 4:1, 4:1.5
16 and 4:2 for the Ni-Co/Al₂O₃ catalyst and 4:0, 4:0.5, 4:1, 4:2 and 4:3 for the Ni-
17 Mg/Al₂O₃ catalyst. The results obtained demonstrated that the catalysts and the
18 CO₂/steam ratio influence the syngas quality, as represented by the H₂/CO molar ratio
19 value. With the Ni-Co/Al₂O₃ catalyst, the H₂/CO molar ratio was increased from 0.74
20 (no steam) to 0.94 (CO₂:steam ratio; 4:1) however the H₂/CO molar ratio decreased
21 with further steam addition. Results using the Ni-Mg/Al₂O₃ catalyst showed a different
22 trend, wherein the H₂/CO molar ratio increased with the increase of steam addition into
23 the system. From the evaluation of the gas composition, the steam addition with the Ni-
24 Mg/Al₂O₃ catalyst promoted hydrogen production while the Ni-Co/Al₂O₃ catalyst
25 promoted carbon monoxide production. The addition of steam to the dry reforming of
26 waste plastics has the potential to manipulate the H₂/CO molar ratio hence, the quality
27 of syngas produced can be matched to the desired end-use industrial application.

28
29 **Keywords:** Waste; Plastics; Reforming; Carbon dioxide; Steam; Catalyst

1 **1. Introduction**

2

3 There is current interest in the production of alternative feedstock sources for
4 the production of synthesis gas (syngas) composed of mainly hydrogen and carbon
5 monoxide. Much of the research has focused on steam reforming or co-gasification
6 processes with air and steam [1-5]. However, there are fewer reports that have
7 investigated the dry reforming (CO₂ reforming) process [6]. The dry reforming process
8 for producing syngas requires a hydrocarbon source, and waste plastics represents a
9 novel potential hydrocarbon feedstock since they are rich in CH-CH molecular chains.
10 Therefore, the dry reforming of waste plastics alleviates a problematic waste treatment
11 issue and also utilises carbon dioxide which is a greenhouse gas and subject to intense
12 research in regard to CO₂ capture and storage/utilisation processes.

13 The uses of syngas include producing methanol, ammonia and synthetic fuel
14 through Fischer-Tropsch synthesis. The selection of the particular H₂/CO molar ratio is
15 considered critical to match with the end-use product processing requirements [7-10].
16 Several studies on dry reforming of methane suggested that the addition of steam and/or
17 oxygen were advantageous in controlling the H₂/CO molar ratio [11-14]. The H₂/CO
18 ratio of methane dry reforming is unity, while the H₂/CO ratio of steam reforming is
19 about four, hence the mixture of both produced a desired H₂/CO ratio for the Fischer-
20 Tropsch process [15]. Furthermore, the addition of steam and/or oxygen may also act
21 as a coke gasifier in the reforming process. Edreis et al. reported in their study on CO₂
22 co-gasification of petroleum coke and sugar cane bagasse that the char gasification
23 occurred at the temperature more than 700 °C [16]. Moreover, the use of suitable
24 catalysts further enhances the reforming process and can improve the coke resistance
25 ability [17-20]. Whilst there is research into the combination of dry reforming and steam

1 reforming of methane, there are few studies investigating the combination of dry and
2 steam reforming for the processing of waste plastics.

3 Previously we have reported that a Ni-Co/Al₂O₃ catalyst had high catalytic
4 activity towards the dry reforming of waste high density polyethylene for syngas
5 production [21]. In addition, no detectable carbon was formed on the catalyst during
6 dry reforming. In this study, the use of both carbon dioxide and steam in the reforming
7 process have been investigated with the aim of controlling the H₂/CO molar ratio as
8 well as syngas yield. The catalyst used was the Ni-Co/Al₂O₃ catalyst as used before,
9 but the results were also compared with a different catalyst, Ni-Mg/Al₂O₃. This work
10 is also a continuation of our previous work on the influence of steam on non-catalytic-
11 CO₂ reforming of HDPE [22].

12

13 **2. Materials and methods**

14

15 2.1 Materials.

16

17 A blended mixture of different plastics was prepared based on the typical
18 composition of the plastics found in municipal solid waste [23]. The mixture consisted
19 of, low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene
20 (PS), polyethylene terephthalate (PET) and polypropylene (PP) and the composition
21 was, 42 wt.% of LDPE, 20 wt.% of HDPE, 16wt.% of PS, 12 wt.% of PET and 10wt.%
22 of PP. In this report, the plastics mixture was designated as simulated mixed waste
23 plastics (SWP).

24 Two types of catalysts were used in the investigation; Ni-Co/Al₂O₃ and Ni-
25 Mg/Al₂O₃. Ni-Co/Al₂O₃ was shown to be effective for the dry reforming of plastics on

1 our previous study [21] while Ni-Mg/Al₂O₃ was selected based on its high catalytic
2 activity for the steam reforming process [24-26]. Both catalysts were prepared by the
3 rising-pH technique [27] by first mixing nickel (II) nitrate hexahydrate and aluminium
4 nitrate nonahydrate with deionised water. Either cobalt (II) nitrate hexahydrate or
5 magnesium nitrate hydrate was also mixed into the solution. After two hours of
6 moderate stirring at 40 °C, 1 M ammonium precipitant was added into the aqueous
7 solution until a pH of 8.3 was reached. The precipitates were then filtered, dried and
8 calcined at 750 °C and sieved to a particle size of 50 – 212 µm. The characterization of
9 fresh Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ were discussed in detail in our previous paper [21],
10 but briefly, the catalysts consisted of Ni-Co-Al with a molar ratio of 1:1:1 and Ni-Mg-
11 Al, also with a molar ratio of 1:1:1 with BET surface areas of 48 m² g⁻¹ and 66 m² g⁻¹
12 respectively.

13

14 2.2 Experimental system.

15

16 The catalytic-steam/dry reforming of mixed waste plastics over Ni-Co/Al₂O₃
17 and Ni-Mg/Al₂O₃ catalysts was carried out in a two-stage fixed bed reactor and the
18 details of the reactor and experimental procedure is covered in our previous studies [21,
19 22]. The two-stages consisted of pyrolysis of the plastics at 500 °C to produce the
20 hydrocarbons which were then reformed with CO₂/steam at 800 °C in the second
21 catalyst stage reactor. The size of the reactor was 60 cm in length with 2.5 cm inner
22 diameter and constructed of Inconel. 2 g of plastic sample and 1 g of catalyst were used.
23 The CO₂/steam ratios of 4:0, 4:0.5, 4:1, 4:1.5 and 4:2 were used for the Ni-Co/Al₂O₃
24 catalyst and for the Ni-Mg/Al₂O₃ catalyst, the CO₂/steam ratios used were 4:0, 4:0.5,
25 4:1, 4:2 and 4:3. The Ni-Mg/Al₂O₃ catalyst showed very small differences with the

1 steam/CO₂ ratio of 4:1.5 (results not shown here), hence the ratio was increased up to
2 4:3. The CO₂ and/or steam was fed directly into the second catalytic stage of the reactor
3 system. Nitrogen was used as a carrier gas for the entire process with a flow rate of 200
4 ml min⁻¹. The product gases were passed through a three-stage condenser system where
5 any condensed oil/wax/unreacted water was trapped. However, during the
6 investigation, no condensed oil/wax products in the condensation system were detected.
7 This was due to the high temperature of the second stage reactor, 800 °C, where the
8 catalyst was placed. The quantity of water that was consumed during reactions was
9 calculated by difference via the quantity of water injected (syringe pump) and quantity
10 of unreacted water (condensers). The non-condensed gases were collected in a Tedlar™
11 sample bag and analysed by gas chromatography as detailed previously [21, 22]. CO₂
12 conversion was measured by difference; the total amount of CO₂ introduced into the
13 system and unreacted/produced CO₂ (left in the sample gas bag). It should be noted that
14 CO₂ might also be produced during the gasification/reforming process. In addition, the
15 weight of liquid, char and carbon deposition were determined by the difference before
16 and after experimentation of the condensers, sample holder and reactor tube
17 respectively.

18 After experimentation, the catalyst was removed and any carbonaceous coke
19 deposited on the catalyst surface was analysed by scanning electron microscopy (SEM),
20 X-Ray Diffraction (XRD) and temperature programmed oxidation (TPO). The
21 morphology of the carbon deposits on the catalyst were determined by a Hitachi
22 SU8230 high resolution SEM. The XRD analysis was conducted using a Bruker D-8
23 diffractometer and the pattern identification was obtained by HighScore Plus Software.
24 For the TPO experiments, 10 mg of reacted catalyst was heated from ambient
25 temperature to 800 °C under air atmosphere with a thermogravimetric analyser (TGA-

1 50 Shimadzu). The deposited carbon was calculated based on weight difference of the
2 reactor before and after the experiment. In addition, from SEM and TPO data, the same
3 trend in deposited carbon on the catalyst surface was observed.

4

5 **3. Results and discussion**

6

7 3.1 Product yields.

8

9 Table 1 and Table 2 show the product yields from the catalytic-dry/steam
10 reforming of the simulated mixture of LDPE, HDPE, PS, PET and PP in relation to the
11 CO₂/steam reforming gas ratio with the Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ catalysts
12 respectively. The product yield calculations can be expressed by the following formulae:

13

14 *Products yield in relation to plastics, carbon dioxide and reacted water, (wt. %)*
15
$$= \frac{W_{Product}}{W_{swp} + W_{CO2input} + W_{steaminput}} \times 100$$

16

17

18 *Products yield in relation to plastics only, (wt. %) carbon dioxide and reacted water, (wt. %)*
19
$$= \frac{W_{Product}}{W_{swp}} \times 100$$

20

21 The total gas yield in relation to all of the reactants (plastic, carbon dioxide and
22 reacted water) reached the maximum point of 94.58 wt.% at the CO₂/steam ratio of
23 4:1.5. However, calculation of the total gas yield in relation to only the mass of plastic
24 used in the experiments showed an increase from ~268 wt.% to 356 wt.% as the
25 CO₂/steam ratio was increased. The reforming gases CO₂ and steam clearly
26 contributing to the total gas product yield in addition to the hydrocarbons from the

1 plastic pyrolysis-catalysis. The residue of the simulated mixed waste plastics after the
2 experiment in the sample holder remained unchanged at 3.0 wt.%_{plastic only}. Increasing
3 the CO₂/steam ratio produced a large impact on the amount of carbon deposited on the
4 catalyst, showing a decrease from 23.50 wt.%_{plastic only} with the experiment without
5 steam addition, to 0.50 wt.%_{plastic only} at the CO₂/steam ratio of 4:2.

6 Similar trends of syngas yield corresponding to the mass of simulated mixed
7 waste plastic were also shown from the experiments with the Ni-Mg/Al₂O₃ as presented
8 in Table 2. However, the carbon formation on the catalyst during the experiments first
9 decreased with the increase of CO₂/steam ratio and then increased at the higher
10 CO₂/steam ratios.

11

12 3.2 Gas composition.

13

14 The gases contained in the gas sample bag were analysed by gas chromatography
15 and the results for carbon monoxide (CO), hydrogen (H₂), methane (CH₄) and C₂-C₄
16 hydrocarbons from the catalytic-dry/steam reforming of simulated mixed waste plastics
17 over the Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ catalysts are shown in Figure 1. Our previous
18 study [22] demonstrated that the addition of a gasification/reforming stage enhanced the
19 formation of H₂ from the pyrolysis-dry reforming of waste high density polyethylene
20 under a CO₂ atmosphere while the concentration of methane and C₂-C₄ hydrocarbons
21 was markedly reduced from 96 vol.% to only 13 vol.%, suggesting the dominance of
22 the reforming reaction. In addition, based on our previous work [28] which reported gas
23 yields for individual plastics in the absence of CO₂, calculation of the CO yield from
24 SWP could be made based on the CO yield from the individual plastics (LDPE, HDPE,
25 PP, PET and PS) used in the SWP mixture. The results showed that in this work there

1 was a large increase in CO yield when CO₂ was introduced to the system. In the presence
2 of the Ni-Co/Al₂O₃ catalyst, the CO yield increased from 0.14 g g⁻¹_{SWP} to 1.56 g g⁻¹_{SWP}
3 for the CO₂/steam ratio of 4:0 and with the Ni-Mg/Al₂O₃ catalyst the CO yield increased
4 from 0.14 g g⁻¹_{SWP} to 1.81 g g⁻¹_{SWP} at a CO₂/steam ratio of 4:0.

5 In general, the main gases from the catalytic-dry/steam reforming process for
6 both catalysts were carbon monoxide and methane and lower yields of hydrogen and
7 C₂-C₄ hydrocarbons as shown in Figure 1, suggesting the reaction between pyrolytic
8 gases and CO₂ and/or steam occurred in the second stage reactor. These two reactions
9 representing the dry reforming reaction (Equation 1) and the steam reforming reaction
10 (Equation 2).

11



13



15

16 The results obtained for the experiments with the Ni-Co/Al₂O₃ catalyst shown
17 in Figure 1, shows a close relationship between the reactant gases produced from
18 pyrolysis; methane and C₂-C₄ hydrocarbons, and the output gases; carbon monoxide
19 and hydrogen. The decrease in the concentration of CH₄ and C₂-C₄ hydrocarbons
20 corresponding to the reduction in the CO₂/steam input ratio from 4:0 to 4:1.5, resulting
21 in an increase in the product CO and H₂. The relative increase in gas yield was more
22 marked for CO compared to H₂, resulting in a change in the H₂/CO molar ratio. From
23 the discussion previously, the carbon deposits on the catalyst were decreased with the
24 increase in the CO₂/steam ratio. It is suggested that reaction occurred between carbon

1 dioxide/steam and char/fixed carbon as in the following reactions (Equation 3 and
2 Equation 4).

3



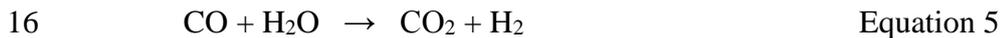
5



7

8 Figure 1 also shows the influence of the CO₂/steam ratio for the reforming of
9 the plastic mixture using the Ni-Mg/Al₂O₃ catalyst. In comparison with the cobalt
10 containing Ni-Co/Al₂O₃ catalyst, the yield of CO was higher, but at higher inputs of
11 steam, the yield of CO fell, with an improved yield of H₂. It is suggested that Ni-
12 Mg/Al₂O₃ also promoted the water gas shift reaction (Equation 5) when more steam
13 was added to the process, hence showing reduction of carbon monoxide yield and
14 increase of hydrogen yield.

15



17

18 3.3 Syngas production and H₂/CO molar ratio.

19

20 Figure 2 shows the relationship between CO₂ conversion, reacted water, syngas
21 yield and H₂/CO molar ratio from the catalytic-dry/steam reforming process of
22 simulated mixed waste plastics over the Ni-Co/Al₂O₃ catalyst. Syngas yield reached its
23 maximum point at the CO₂/steam ratio of 4:1.5 at 159.77 mmol g⁻¹_{SWP}. The maximum
24 peak of CO₂ conversion_{inlet-outlet}, at 56.55 % was also found at the CO₂/steam ratio of

1 4:1.5. The quantity of reacted water increased with the raising of the CO₂/steam ratio
2 to a maximum, which was 0.56 g g⁻¹_{SWP} at the CO₂/steam ratio of 4:2.

3 However, the H₂/CO molar ratio shows a maximum at the CO₂/steam ratio of
4 4:1, producing a H₂/CO molar ratio of 0.94, but decreased as the amount of steam input
5 was increased. This might be due to the large increase in CO production compared to
6 the H₂ yield. This also suggests that the Ni-Co/Al₂O₃ catalyst enhanced the dry
7 reforming reaction (Equation 1) as well as the Boudouard reaction (Equation 3)
8 compared to the steam reforming reaction (Equation 2) hence, there was a high CO
9 yield compared to H₂ yield. Butterman et al. [29] in their study on steam gasification of
10 biomass with the addition of CO₂, also showed that an increase of CO₂ input into the
11 system, enhanced the production of CO with reduced H₂ yield [29].

12 Figure 3 shows the results from the catalytic-dry/steam reforming of simulated
13 mixed waste plastics over the Ni-Mg/Al₂O₃ catalyst. A maximum peak of syngas yield
14 at 147 mmol g⁻¹_{swp} was obtained at the CO₂/steam ratio of 4:1. The CO₂ conversion_{inlet-}
15 _{outlet} and reacted water showing an opposite trend towards each other while the H₂/CO
16 molar ratio showing a similar trend with the reacted water, which increased with the
17 increased CO₂/steam molar ratio. The drop in CO₂ reaction and the rise in steam
18 consumption with the increased of CO₂/steam ratio, suggesting that the Ni-Mg/Al₂O₃
19 might preferentially promote the steam reforming reaction rather than the dry reforming
20 reaction. This further confirmed that the water gas shift reaction (Equation 5) occurred
21 in the second stage reactor among the low molecular weight hydrocarbons (methane),
22 condensable hydrocarbons (C₂-C₄) and steam yielding CO₂ hence, lessening CO₂
23 conversion_{inlet-outlet} but promoting water consumption (reacted water) starting at the
24 CO₂/steam ratio of 4:0.5.

25

1 3.4 Catalyst coke formation.

2

3 The reacted Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ catalysts from the dry/steam reforming
4 experiments with the simulated mixed waste plastics in relation to CO₂/steam feed ratio
5 were characterized by temperature programmed oxidation (TPO). The results of TGA-
6 TPO and DTG-TPO of both reacted catalysts are shown in Figure 4 and Figure 5
7 respectively. As shown in Table 1, the quantity of coke deposited on the Ni-Co/Al₂O₃
8 catalyst showed a significant decrease of 98 % with an increase in the CO₂/steam ratio.
9 This result is in agreement with the TPO experiment, where the catalysts used with
10 higher steam inputs showed little mass loss since there were few deposits of carbon on
11 the catalyst surface available for oxidation (combustion). Therefore it is suggested with
12 the increase of CO₂/steam ratio, more carbon was reacted with either carbon dioxide or
13 steam via Reaction 3 and Reaction 4. It should also be noted that with the reacted Ni-
14 Co/Al₂O₃ catalyst, there was a large increase of mass at around a temperature of 500 °C.
15 Due to the low concentration of coke deposited on the reacted catalysts, it is suggested
16 that the mass gain was due to oxidation of nickel and cobalt metal in the catalyst.
17 Compared to the reacted Ni-Co/Al₂O₃ catalyst, high oxidation temperature peaks
18 (higher than 600 °C) were also observed for reacted Ni-Mg/Al₂O₃ catalyst as shown in
19 Figure 5. Scanning electron microscopy observation of the used catalysts confirmed
20 that only low levels of carbon deposition occurred on the Ni-Co/Al₂O₃ catalyst
21 compared to the Ni-Mg/Al₂O₃ reacted catalyst.

22 The XRD spectra of the fresh catalysts and the used Ni-Co/Al₂O₃ and Ni-
23 Mg/Al₂O₃ catalysts in relation to the different CO₂/steam ratios are shown in Figure 6
24 and Figure 7 respectively. Fewer diffraction peaks were observed from the used Ni-
25 Co/Al₂O₃ catalyst compared to the fresh catalyst. Also the XRD spectra of the used Ni-

1 Co/Al₂O₃ catalysts show a similar profile with the increase of CO₂/steam ratio, however
2 the peak intensity was reduced compared to the fresh catalyst. The NiO crystallite size
3 determined for the fresh Ni-Co/Al₂O₃ catalyst at a 2-Theta value of 43.3° was 93.6 Å.
4 For the used Ni-Co/Al₂O₃ catalysts, Ni and Co metal peaks were detected at 2-Theta
5 values of 44.2° and 51.5° [30], which indicates that the NiO was reduced to its metallic
6 form in-situ by the reducing agents present in the pyrolysis gases and/or produced in
7 the reformer reactor e.g H₂ [31, 32]. The size of the Ni and Co metal peaks (overlapped)
8 was increased for the used catalyst at a 2-Theta of 44.2°, from 471.2 Å at the CO₂/steam
9 ratio of 4:0 to 551.5 Å at the CO₂/steam ratio of 4:1 but was reduced to 493.5 Å at the
10 CO₂/steam ratio of 4:2.

11 However, for the Ni-Mg/Al₂O₃ catalyst, more XRD peaks were observed from
12 the reacted catalyst compared to the fresh Ni-Mg/Al₂O₃ catalyst. MgO peaks were
13 observed for both the fresh and used catalysts. Basagiannis and Verykios [33] suggested
14 that the spillover of O and/or –OH anions from the carrier surface to metal surface is
15 improved with the existence of MgO in the catalyst. A Ni metal peak was observed at
16 a 2-Theta value of about 44.4° and 51.8°. The Ni crystallite size from the XRD peak at
17 a 2-Theta of 44.4° was increased with the increase of CO₂/steam ratio (4:0 at 241.6 Å,
18 4:1 at 276.9 Å and 4:2 at 280.6 Å) and sharper peaks were also observed. The NiO
19 crystallite size for fresh Ni-Mg/Al₂O₃ at a 2-Theta of 43.2° was only 102.9 Å.

20 The results have shown that by changing the CO₂/steam input ratio, the syngas
21 H₂/CO ratio can be manipulated between 0.74 and 0.94 for the Ni-Co/Al₂O₃ catalyst
22 and between 0.6 and 1.4 for the Ni-Mg/Al₂O₃ catalyst. The optimum ratio of H₂/CO
23 required for onward process utilisation depends on the application. Majewski and
24 Wood [34] have reported that a H₂/CO ratio between 1.7 – 2.15 can be used for Fischer
25 Tropsch processing for the production of liquid hydrocarbon fuels, depending on the

1 type of catalyst used and the process conditions. A H₂/CO ratio between 1.5 – 2 can
2 also be used for the production of methanol or for dimethyl-ether synthesis. Therefore,
3 the syngas H₂/CO ratio derived from waste plastics reported here would require
4 supplemental hydrogen addition to raise the H₂/CO ratio for use in such applications.
5 Alternatively, the different catalysts used here have been shown to alter the H₂/CO ratio
6 by using different metal promoters. There is therefore scope for further research on
7 different types of catalyst to also manipulate the product syngas H₂/CO ratio.

8

9 **4. Conclusions**

10

11 Incorporating steam into the dry reforming process was investigated in order to
12 manipulate the H₂/CO molar ratio for end-use industrial applications. The results
13 showed that by changing the CO₂/steam feed ratio, as well as suitable catalyst selection,
14 the syngas production and H₂/CO molar ratio could be varied.

15 For the catalytic-dry/steam reforming of simulated mixed waste plastics over
16 Ni-Co/Al₂O₃ catalyst, it is suggested that the optimum CO₂/steam ratio was observed
17 at 4:1. At this ratio, the highest H₂/CO molar ratio was observed at 0.94 and an
18 acceptable syngas yield was also obtained at 133.87 mmol_{syngas} g⁻¹_{swp}. For the reforming
19 process over the Ni-Mg/Al₂O₃ catalyst, the optimum syngas production of 146.77
20 mmol_{syngas} g⁻¹_{swp} was observed at the CO₂/steam ratio of 4:1.

21 It is also suggested that the Ni-Co/Al₂O₃ catalyst enhanced the dry reforming
22 reaction and Bourdouard reaction (Equation 1 and 3) hence, high CO and high syngas
23 yield was obtained. In the case of the Ni-Mg/Al₂O₃ catalyst, the process was
24 preferentially promoted towards the steam reforming and water gas shift reactions
25 (Equation 2 and 5) hence, higher H₂ yield and higher H₂/CO molar ratios were obtained.

1 In addition, increasing the CO₂/steam ratio with the Ni-Mg/Al₂O₃ catalyst showed an
2 undesirable carbon build-up on the catalyst during the experiments.

3

4 **Acknowledgements**

5

6 The authors are grateful for the financial support of the Majlis Amanah Rakyat
7 (MARA) Malaysia (PhD scholarship for Juniza MD Saad) and the University of Leeds.

8 The authors also thank Dr. Mohamad Anas Nahil for his assistance.

9 This project has received funding from the European Union's Horizon 2020
10 research and innovation programme under the Marie Skłodowska-Curie grant
11 agreement No. 643322 (FLEXI-PYROCAT).

12

13

1 **References**

- 2
- 3 [1] K. Kumabe, T. Hanaoka, S. Fujimoto, T. Minowa, K. Sakanishi. Co-gasification
4 of woody biomass and coal with air and steam. *Fuel* 86 (2007) 684-689.
- 5 [2] G. Ruoppolo, P. Ammendola, R. Chirone, F. Miccio. H₂-rich syngas production
6 by fluidized bed gasification of biomass and plastic fuel. *Waste Manage.* 32 (2012)
7 724-732.
- 8 [3] N. Nipattummakul, I.I. Ahmed, S. Kerdsuwan, A.K. Gupta. Steam gasification of
9 oil palm trunk waste for clean syngas production. *Appl. Energ.* 92 (2012) 778-782.
- 10 [4] R.A. Moghadam, S. Yusup, Y. Uemura, B.L.F. Chin, H.L. Lam, A. Al Shoaibi.
11 Syngas production from palm kernel shell and polyethylene waste blend in
12 fluidized bed catalytic steam co-gasification process. *Energy* 75 (2014) 40-44.
- 13 [5] I.I. Ahmed, N. Nipattummakul, A.K. Gupta. Characteristics of syngas from co-
14 gasification of polyethylene and woodchips. *Appl. Energ.* 88 (2011) 165-74.
- 15 [6] H. Yamada, H. Mori, T. Tagawa. CO₂ reforming of waste plastics. *J. Ind. Eng.*
16 *Chem.* 16 (2010) 7-9.
- 17 [7] J. Wu, Y. Fang, Y. Wang, D.K. Zhang. Combined coal gasification and methane
18 reforming for production of syngas in a fluidized-bed reactor. *Energy Fuels* 19
19 (2005) 512-516.
- 20 [8] Z. Ravaghi-Ardebili. F. Manenti, C. Pirola, F. Soares, M. Corbetta, S. Pierucci, E.
21 Ranzi. Influence of the effective parameters on H₂:CO ratio of syngas at low-
22 temperature gasification. *Chem. Eng. Trans.* 37 (2014) 253-258.
- 23 [9] B.B. Sahoo, N. Sahoo, U.K. Saha. Effect of H₂:CO ratio in syngas on the
24 performance of a dual fuel diesel engine operation. *Appl. Therm. Eng.* 49 (2012)
25 139-146.
- 26 [10] Y. Cao, Z. Gao, J. Jin, H. Zhou, M. Cohron, H. Zhao, H. Liu, W. Pan. Synthesis
27 gas production with an adjustable H₂/CO ratio through the coal gasification
28 process: Effects of coal ranks and methane addition. *Energy Fuels* 22 (2008) 1720-
29 1730.
- 30 [11] V.R. Choudhary, K.C. Mondal. CO₂ reforming of methane combined with steam
31 reforming or partial oxidation of methane to syngas over NdCoO₃ perovskite-type
32 mixed metal-oxide catalyst. *Appl. Energy* 83 (2006) 1024-1032.
- 33 [12] L.C.S. Kahle, T. Roussière, L. Maier, K. Herrera-Delgado, G. Wasserschaff, S.A.
34 Schunk, eO. Deutschmann. Methane dry reforming at high temperature and
35 elevated pressure: Impact of gas-phase reactions. *Ind. Eng. Chem. Res.* 52 (2013)
36 11920-11930.
- 37 [13] M. Rieks, R. Bellinghausen, N. Kockmann, L. Mleczko. Experimental study of
38 methane dry reforming in an electrically heated reactor. *Int. J. Hydrogen Energ.* 40
39 (2015) 15940-15951.

- 1 [14] C. Song, W. Pan. Tri-reforming of methane: a novel concept for catalytic
2 production of industrially useful synthesis gas with desired H₂/CO ratios. *Catal.*
3 *Today*. 98 (2004) 463-484.
- 4 [15] W.L. Luyben. Control of parallel dry methane and steam methane reforming
5 processes for Fischer–Tropsch syngas. *J. Process Control* 39 (2016) 77-87.
- 6 [16] Edreis EMA, Luo G, Li A, Chao C, Hu H, Zhang S, et al. CO₂ co-gasification of
7 lower sulphur petroleum coke and sugar cane bagasse via TG–FTIR analysis
8 technique. *Bioresource Technology*. 2013;136:595-603.
- 9 [17] S.A. Theofanidis, R. Batchu, V.V. Galvita, H. Poelman, G.B. Marin. Carbon
10 gasification from Fe–Ni catalysts after methane dry reforming. *Appl. Catal. B-*
11 *Environ*. 185 (2016) 42-55.
- 12 [18] E. Baktash, P. Littlewood, R. Schomäcker, A. Thomas, P.C. Stair. Alumina
13 coated nickel nanoparticles as a highly active catalyst for dry reforming of
14 methane. *Appl. Catal. B-Environ*. 179 (2015) 122-127.
- 15 [19] M.M. Makri, M.A. Vasiliades, K.C. Petallidou, A.M. Efstathiou. Effect of
16 support composition on the origin and reactivity of carbon formed during dry
17 reforming of methane over 5 wt% Ni/Ce_{1-x}MxO_{2-δ} (M = Zr⁴⁺, Pr³⁺) catalysts.
18 *Catal. Today* 259 (2016) Part 1:150-164.
- 19 [20] H. Ay, D. Üner. Dry reforming of methane over CeO₂ supported Ni, Co and Ni–
20 Co catalysts. *Appl. Catal. B-Environ*. 179 (2015) 128-138.
- 21 [21] J.M. Saad, M.A. Nahil, C. Wu, P.T. Williams. Influence of nickel-based catalysts
22 on syngas production from carbon dioxide reforming of waste high density
23 polyethylene. *Fuel Proc. Technol*. 138 (2015) 156-163.
- 24 [22] J.M. Saad, M.A. Nahil, P.T. Williams. Influence of process conditions on syngas
25 production from the thermal processing of waste high density polyethylene. *J.*
26 *Anal. Appl. Pyrolysis* 113 (2014) 35-40.
- 27 [23] C. Delgado, L. Barrueta, O. Salas, O. Wolf. Assessment of the
28 Environmental Advantages and Drawbacks of Existing and Emerging Polymers
29 Recovery Processes JRC37456. Brussels: European Joint Research Centre; 2007.
- 30 [24] R. Guil-Lopez, R.M. Navarro, A.A. Ismail, S.A. Al-Sayari, J.L.G. Fierro.
31 Influence of Ni environment on the reactivity of Ni–Mg–Al catalysts for the
32 acetone steam reforming reaction. *Int. J. Hydrogen Energ*. 40 (2015) 5289-5296.
- 33 [25] M.L. Dieuzeide, V. Iannibelli, M. Jobbagy, N. Amadeo. Steam reforming of
34 glycerol over Ni/Mg/γ-Al₂O₃ catalysts. Effect of calcination temperatures. *Int. J.*
35 *Hydrogen Energ*. 37 (2012) 14926-14930.
- 36 [26] A.J. Vizcaíno, P. Arena, G. Baronetti, A. Carrero, J.A. Calles, M.A. Laborde, N.
37 Amadeo. Ethanol steam reforming on Ni/Al₂O₃ catalysts: Effect of Mg addition.
38 *Int. J. Hydrogen Energ*. 33 (2008) 3489-3492.

- 1 [27] L. Garcia, A. Benedicto, E. Romeo, M.L. Salvador, J. Arauzo, R. Bilbao.
2 Hydrogen production by steam gasification of biomass using Ni-Al coprecipitated
3 catalysts promoted with magnesium. *Energy Fuels* 16 (2002) 1222-1230.
- 4 [28] J.M. Saad, P.T. Williams. Pyrolysis-catalytic-dry reforming of waste plastics and
5 mixed waste plastic for syngas production. *Energy & Fuels*, 30 (2016), 3198-3204.
- 6 [29] H.C. Butterman, M.J. Castaldi. CO₂ as a carbon neutral fuel source via enhanced
7 biomass gasification. *Env. Sci. Technol.* 43 (2009) 9030-9037.
- 8 [30] E. Horvath, K. Baan, E. Varga, A. Oszko, A. Vago, M. Toro, A. Erdohelyi. Dry
9 reforming of CH₄ on Co/Al₂O₃ catalysts reduced at different temperatures.
10 *Catalysis Today*. (2016). doi:10.1016/j.cattod.2016.04.007.
- 11 [31] J. C. Acomb, C. Wu, P. T. Williams. Control of steam input to the pyrolysis-
12 gasification of waste plastics for improved production of hydrogen or carbon
13 nanotube. *Applied Catalysis B: Environmental*. 147 (2014) 571-584.
- 14 [32] J. C. Acomb, C. Wu, P. T. Williams. The use of different metal catalyst for the
15 simultaneous production of carbon nanotubes and hydrogen from pyrolysis of
16 plastic feedstock. *Applied Catalysis B: Environmental*. 180 (2016) 497-510.
- 17 [33] A.C. Basagiannis AC, X.E. Verykios. Steam reforming of the aqueous fraction of
18 bio-oil over structured Ru/MgO/Al₂O₃ catalyst. *Catalysis Today*. 127 (2007) 256-
19 264
- 20 [34] A.J. Majewski, J. Wood. Tri-reforming of methane over Ni@SiO₂ catalyst. *Int.*
21 *J. Hydrogen Energ.* 39 (2014)12578-12585.

22
23

1 **Table 1:** Product yield distribution from catalytic-dry/steam reforming of simulated
 2 mixed waste plastics over Ni-Co/Al₂O₃ catalyst at the gasification temperature of
 3 800 °C
 4

CO₂/steam ratio	(4:0)	(4:0.5)	(4:1)	(4:1.5)	(4:2)
Product yield in relation to plastic + carbon dioxide + reacted water (wt. %)					
Gas	89.32	88.66	89.76	94.58	89.76
Residue	1.00	0.96	0.86	0.82	0.76
Carbon deposition	7.83	6.85	0.29	0.14	0.13
Mass balance	98.15	96.47	90.91	95.54	90.65
Product yield in relation to plastics only (wt.%)					
Gas	267.95	278.39	314.16	347.58	356.35
Residue	3.00	3.00	3.00	3.00	3.00
Carbon deposition	23.50	21.50	1.00	0.50	0.50
Mass balance	295.45	302.89	318.16	351.08	359.85

5

1 **Table 2:** Product yield distribution from catalytic-dry/steam reforming of simulated
 2 mixed waste plastics over Ni-Mg/Al₂O₃ catalyst at the gasification temperature of
 3 800 °C
 4

CO₂/steam ratio	(4:0)	(4:0.5)	(4:1)	(4:2)	(4:3)
Product yield in relation to plastic + carbon dioxide + reacted water (wt. %)					
Gas	87.46	90.43	95.12	96.31	100.16
Residue	1.00	0.97	0.86	0.86	0.86
Carbon deposition	8.33	6.46	1.28	1.85	4.14
Mass balance	96.79	97.86	97.26	99.02	105.16
Product yield in relation to plastics only (wt.%)					
Gas	262.37	279.89	333.39	337.57	351.06
Residue	3.00	3.00	3.00	3.00	3.00
Carbon deposition	25.00	20.00	4.50	6.50	14.50
Mass balance	290.37	302.89	340.89	347.07	368.56

5

1 **Figure Captions**

2

3 Figure 1. Gas composition for the catalytic-dry/steam reforming of simulated mixed
4 waste plastics (SWP) with different CO₂/steam ratios over Ni-Co/Al₂O₃ and Ni-
5 Mg/Al₂O₃ catalysts

6

7 Figure 2. Syngas yield, H₂/CO molar ratio, reacted water and CO₂ conversion derived
8 from the dry/steam reforming process over Ni-Co/Al₂O₃ catalyst

9

10 Figure 3. Syngas yield, H₂/CO molar ratio, reacted water and CO₂ conversion derived
11 from the dry/steam reforming process over Ni-Mg/Al₂O₃ catalyst

12

13 Figure 4. TGA-TPO and DTG-TPO analysis of catalysts after pyrolysis-dry/steam
14 reforming of simulated mixed waste plastics over the Ni-Co/Al₂O₃ catalyst.

15

16 Figure 5. TGA-TPO and DTG-TPO analysis of catalysts after pyrolysis-dry/steam
17 reforming of simulated mixed waste plastics over the Ni-Mg/Al₂O₃ catalyst.

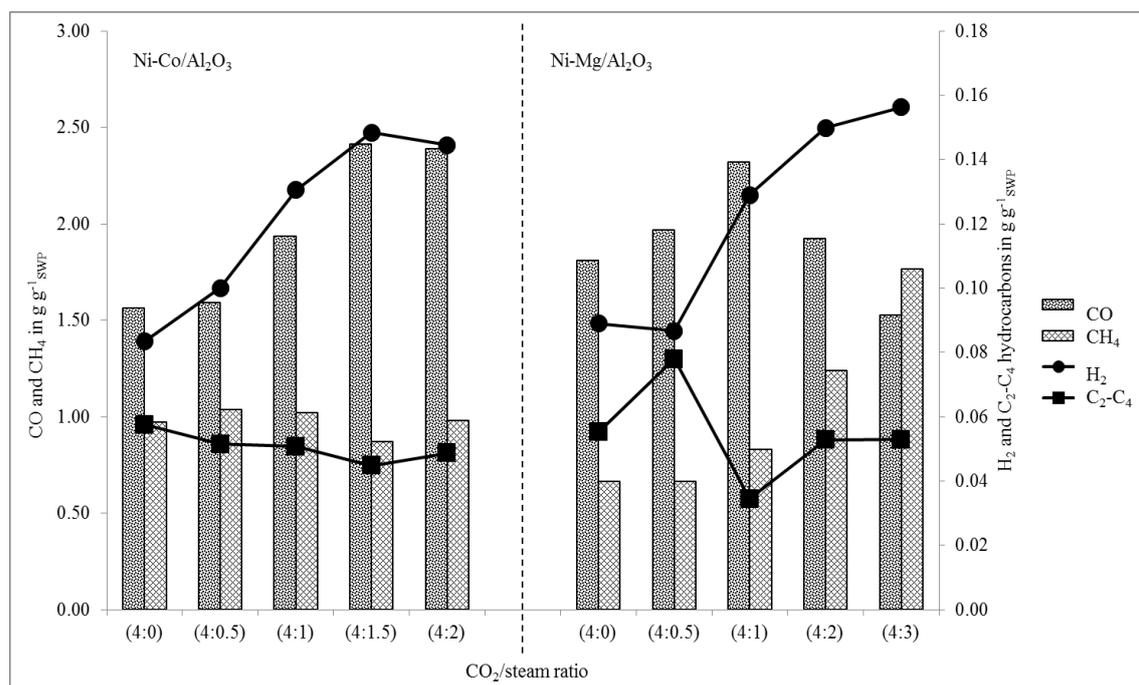
18

19 Figure 6. XRD spectra patterns of catalysts after pyrolysis-dry/steam reforming of
20 simulated mixed waste plastics over the Ni-Co/Al₂O₃ catalyst.

21

22 Figure 7. XRD spectra patterns of catalysts after pyrolysis-dry/steam reforming of
23 simulated mixed waste plastics over the Ni-Mg/Al₂O₃ catalyst.

1



2

3

4

Figure 1

1

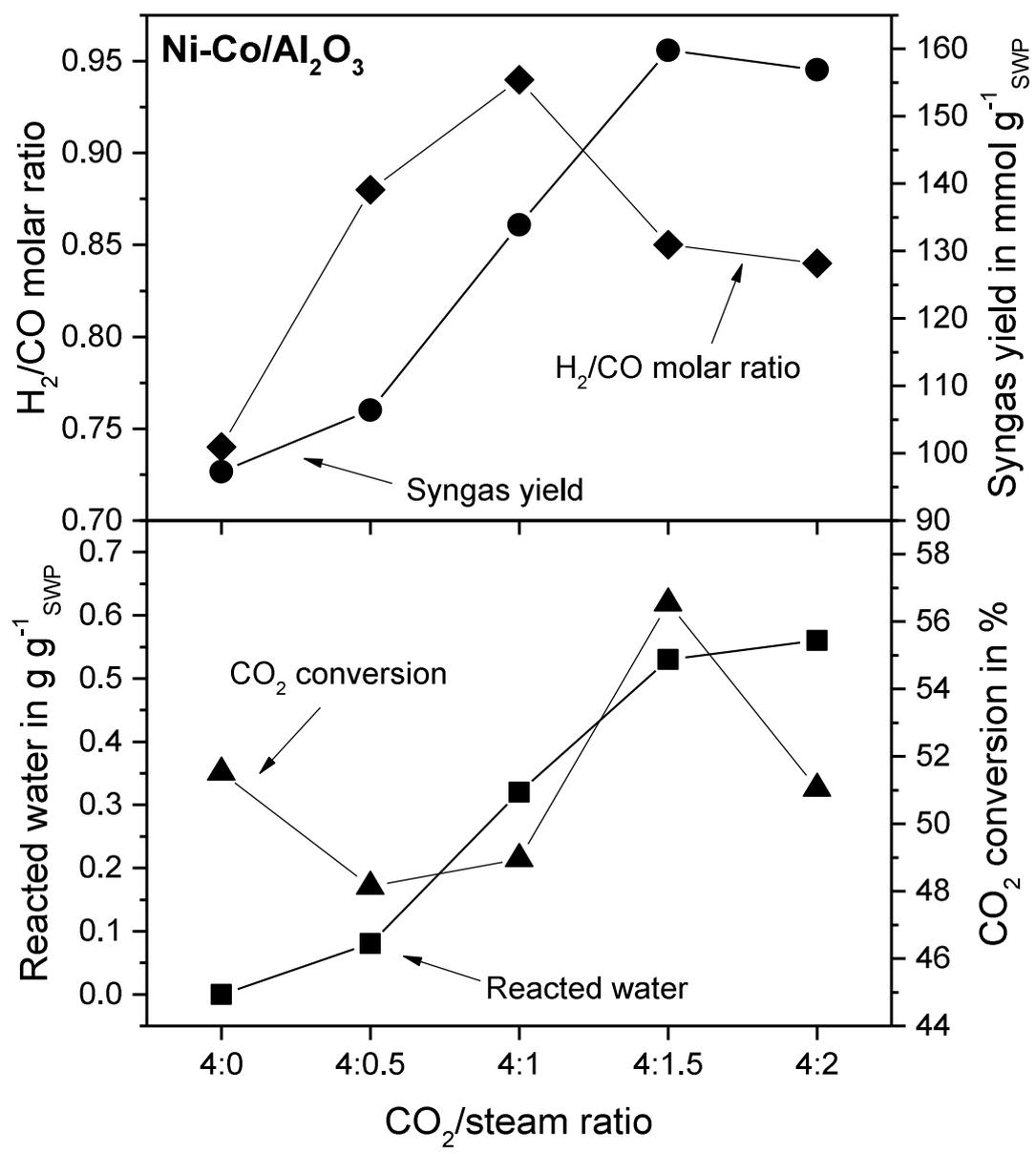


Figure 2

2

3

4

1

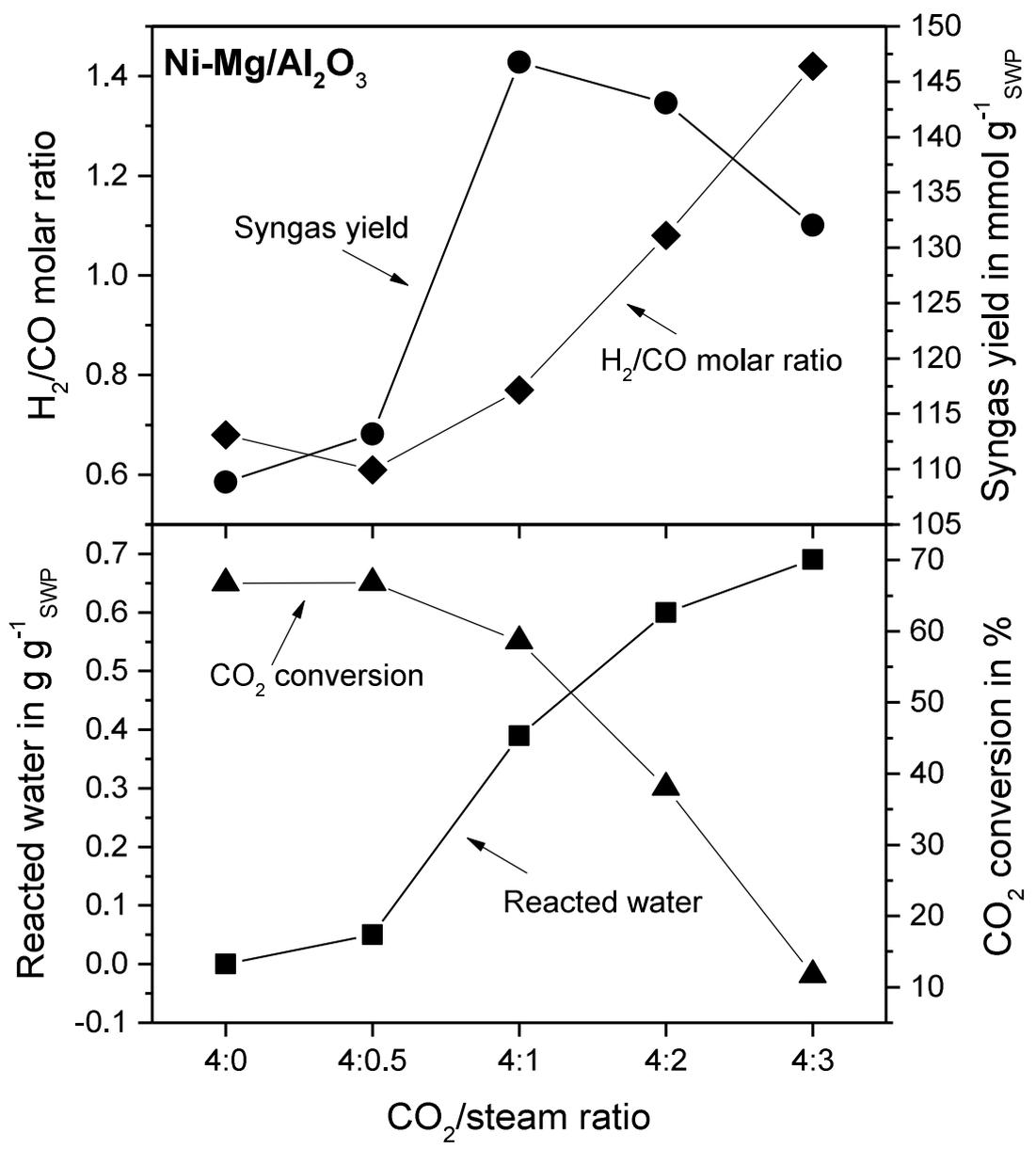


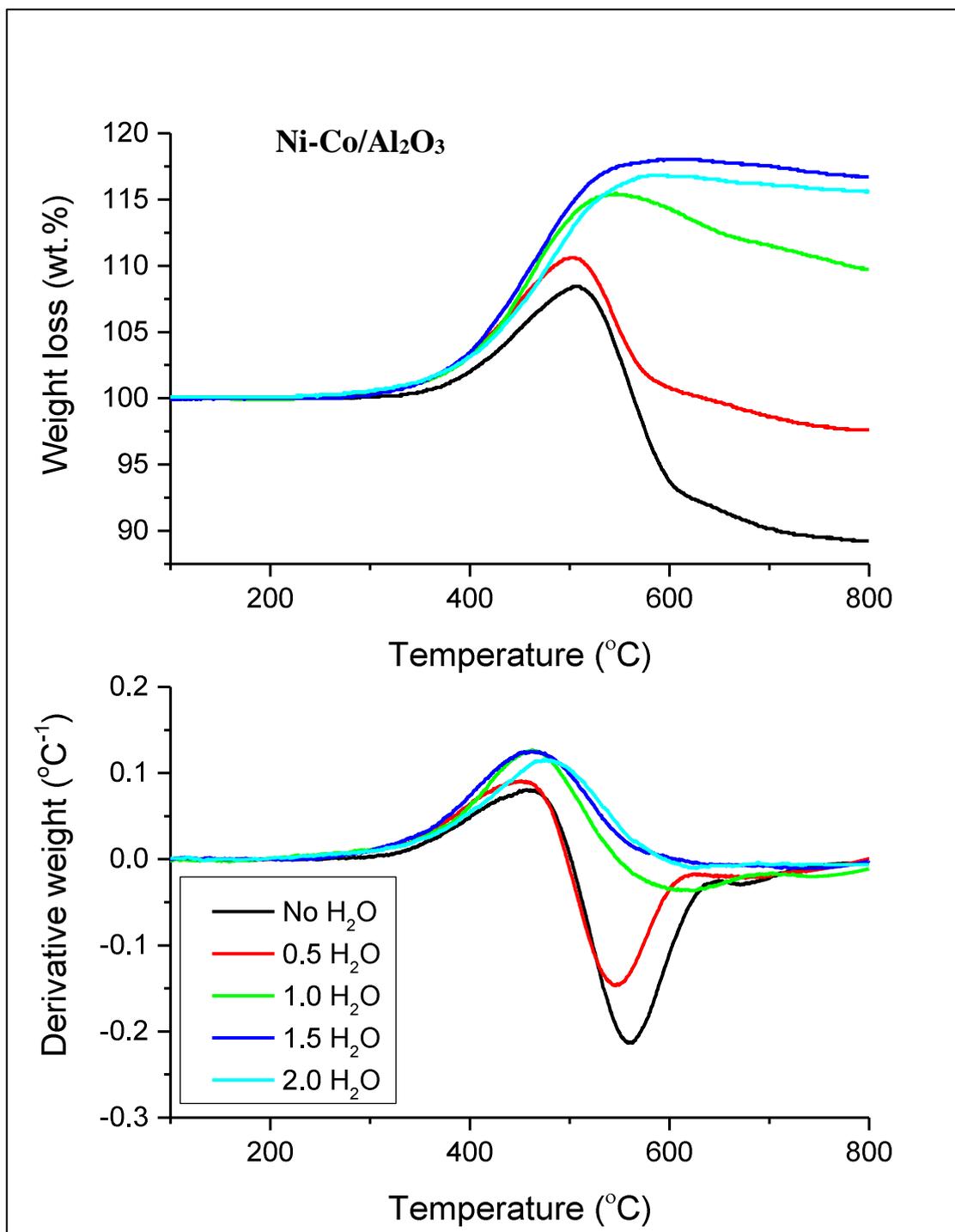
Figure 3

2

3

4

1



2

3

Figure 4

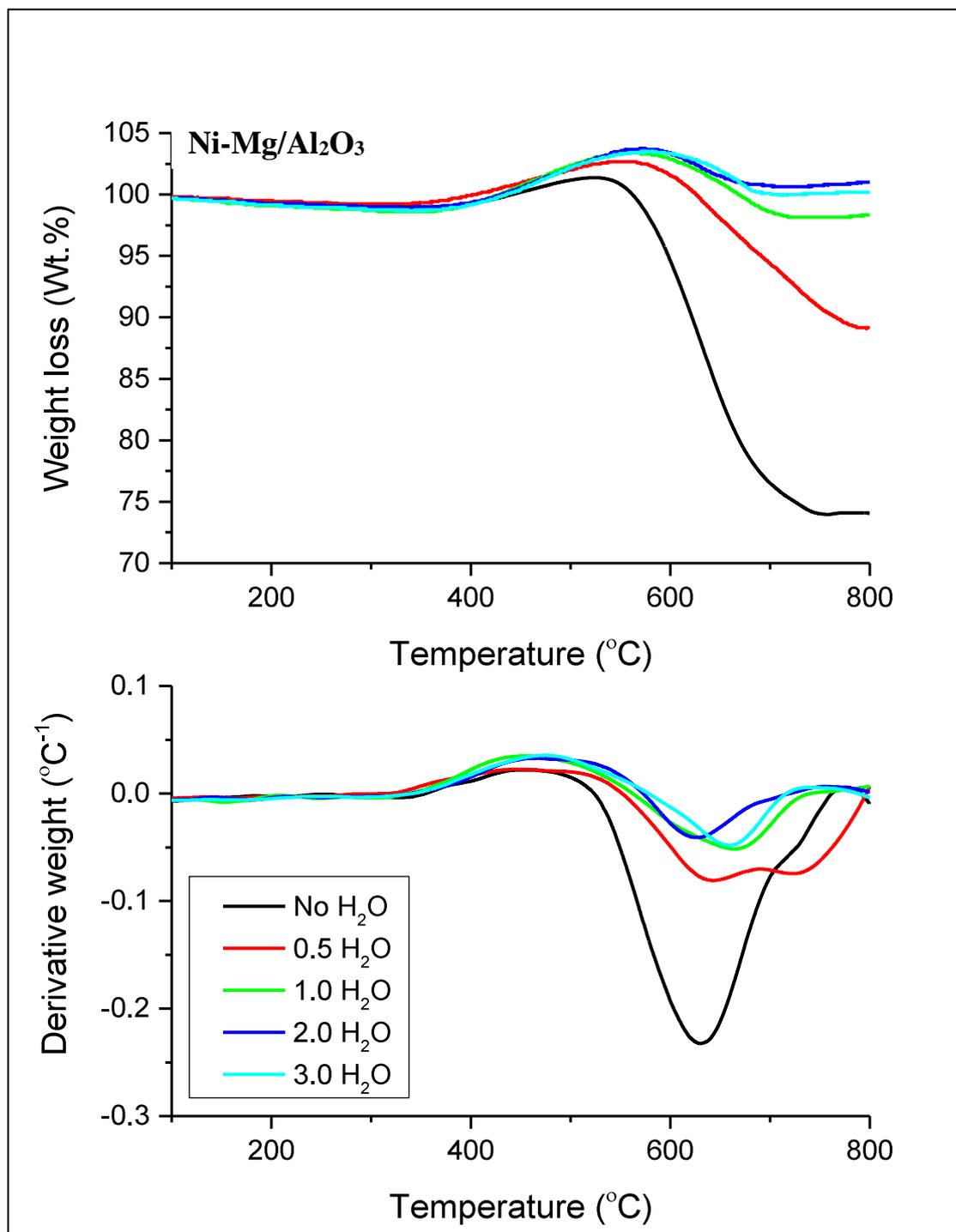


Fig.5

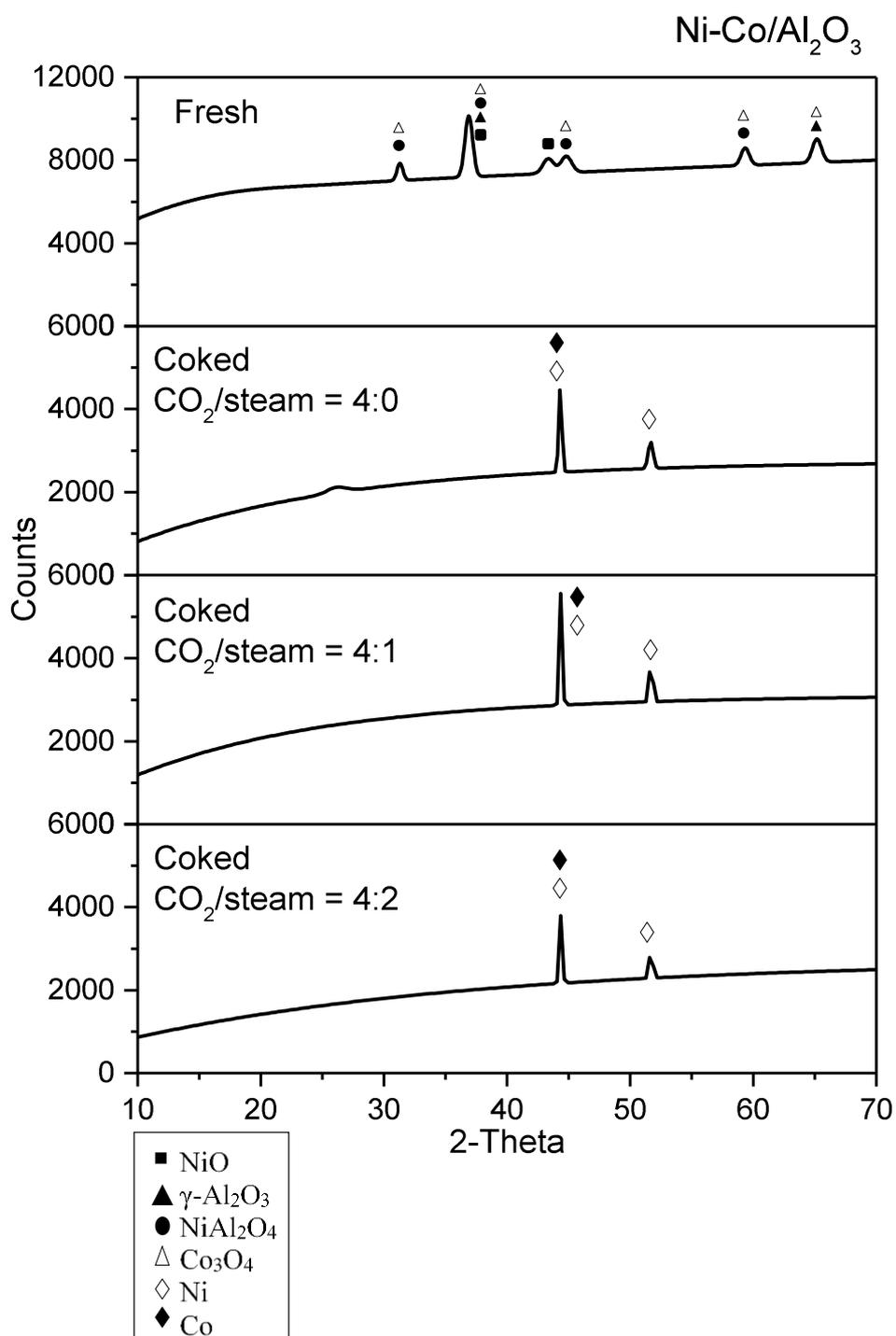


Fig.6

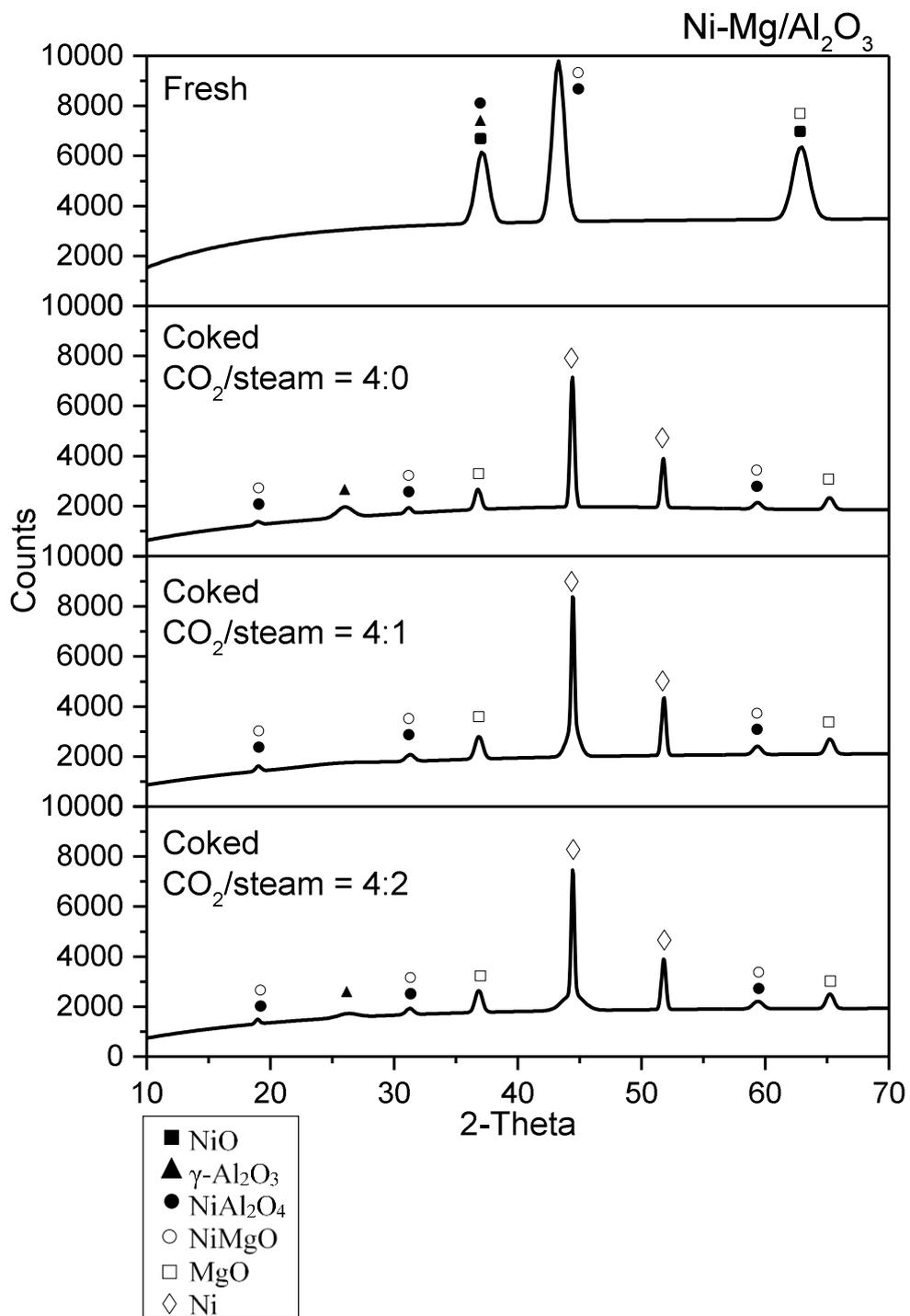


Fig.7