Article

Carbon Formation in the Reforming of Simulated Biomass Gasification Gas on Nickel and Rhodium Catalysts

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Abstract: Biomass gasification gas contains hydrocarbons that must be converted to CO and H₂ prior to the utilization of the gas in a synthesis unit. Autothermal or steam reforming operating with a nickel or noble metal catalyst is a feasible option to treat the gas, but the harsh reaction conditions may lead to the formation of solid carbon. This study discusses the effects of pressure, time-on-stream, and ethylene content on the carbon formation on nickel and rhodium catalysts. The experiments were carried out with laboratory-scale equipment using reaction conditions that were closely simulated after a pilot-scale biomass gasifier. The results indicated that ethylene content above 20,000 vol-ppm and the increased pressure would increase the carbon formation, although there were differences between the rhodium and nickel catalysts. However, carbon formation was significantly more pronounced on the nickel catalyst when the reaction time was increased from 5 h to 144 h. The type of carbon was found to be primarily encapsulating and graphitic. The formation of whisker carbons (also known as carbon nanotubes) was not observed, which is consistent with the literature as the feed gas contained H₂S. It was concluded that utilizing a noble metal catalyst as the front layer of the catalyst bed could lower the risk for carbon formation sufficiently to provide stable long-term operation.

Keywords: autothermal reforming; steam reforming; carbon formation; whisker carbon; encapsulating carbon; nickel catalyst; rhodium catalyst; biomass gasification

1. Introduction

Gasification is one of the technology options for converting biomass into renewable fuels and chemicals [1–4]. In the gasification, the biomass partially oxidizes at 800–1000 °C to form synthesis gas, which contains carbon monoxide and hydrogen as the primary desired components but also impurities such as ash, hydrocarbons, tar, NH₃ and H₂S [5,6]. The actual composition of the product gas and the concentrations of the impurities depend on the biomass feed, the gasifier type and the gasification conditions [5] but in any case, they can lead to operational problems such as catalyst deactivation, coke formation, and tar condensation in the downstream units.

One of the major potential applications for biomass-derived synthesis gas utilization is Fischer–Tropsch synthesis, which combines carbon monoxide with hydrogen to produce hydrocarbon components suitable for transportation fuels and chemicals [1,3,7,8]. Fischer–Tropsch synthesis is very sensitive to any impurities in the feed gas. To reach the required quality, the biomass gasification gas is ultra-cleaned in several steps, including particulate filtration, catalytic steam or autothermal reforming, and removal of sulfur and ammonia [2]. In this study, we focus on the reforming step and especially to its major challenge, carbon formation.

The autothermal and steam reforming of natural gas are well-established industrial processes [9], but in the case of biomass gasification gas, the reformer has to withstand 50–200 vol-ppm of H₂S and decompose higher hydrocarbons, including ethylene and

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polyaromatic hydrocarbons (PAHs, tars), even up to coronene [5,10]. Earlier studies [11–13] have shown that to overcome the negative effect of toxic sulfur on the reforming catalyst, the reformer must be operated at a relatively high temperature, typically 800–1000 °C. This exposes the process unit to another hazard: the formation of solid carbon. This study looks at carbon formation from the perspective of the industrial process operation, specifically the effects of catalyst, time-on-stream (TOS), pressure, and ethylene content of gas.

At high temperatures, components like ethylene and aromatics begin to react thermally to form solid carbon, especially when in contact with a local hotspot, such as the surface of a catalyst particle or the reactor wall [9,14]. The different pathways to the formation of solid carbon from hydrocarbons have been widely studied, but to summarize on a general level, there are three main routes relevant to this study: (1) decomposition of hydrocarbons and CO to atomic carbon, which begins to form linear polymer intermediates that further combine into aromatic rings [15–17]; (2) ethylene reaction to radical light hydrocarbons, which in turn form aromatic rings [18–23]; and (3) formation of carbon directly from tar compounds [17,24]. Once the aromatic rings begin to form, the next step is the formation of PAHs, which are precursors for solid carbon [25]. These pathways can take place simultaneously and are both thermally and activated by the catalyst.

Solid carbon can appear in different forms, but the ones appearing in the reaction conditions of this study are amorphous carbon and graphitic carbon. Graphitic carbon is a highly organized structure of connected aromatic rings that form a sheet [26]. Graphitic layers can grow into larger structures that form thin, encapsulating surfaces in the reactor and on the catalyst [9]. These thin layers do not, at least initially, affect the pressure drop, but if the encapsulation of the catalyst particles is significant, a decrease in the catalyst activity can be observed. Graphitic carbon can also grow into a carbon nanotube (a.k.a. whisker carbon) between catalyst support and metal particle [9,26], which quickly leads to the mechanical destruction of the catalyst [9,27,28]. Whisker carbon forms only on specific metals—nickel is the most common one to be used in the reforming [9]. It does not appear at all on noble metal catalysts [9,27]. Although the carbon nanotube growth is an undesired side reaction in the type of process presented in this study, the carbon nanotubes can also be a valuable product. For example, novel research with molten salt reactors utilizes nanotube growth to control carbon formation [29–31]. These types of solutions would provide interesting possibilities in the future to tackle the carbon formation problem of the reforming process.

The more imperfections are in the graphitic structure, the more amorphous the carbon is. Fully amorphous carbon combines interconnected cyclic and linear carbon molecules that do not have a long-range crystalline order [32]. However, partially amorphous carbon may contain paracrystalline graphene layers [33,34], surrounded and connected by non-structural carbon. Soot is primarily amorphous carbon, and when its partial pressure increases, the carbon condensates and finally solidifies around catalyst particles blocking the access of the reaction gas to the active sites and increasing the pressure drop [9]. In our earlier study [35], we observed a complete blockage of a laboratory-scale reactor by condensed carbon after a reforming of biomass gasification gas with nickel catalyst at 870 °C for 150 h. The different options for carbon formation thermally and on the catalyst are summarized in Figure 1.
Generally speaking, carbon formation depends on numerous variables such as catalyst, temperature, pressure, H₂O/C molar ratio of the feed gas, residence time, and the type of hydrocarbons and impurities in the feed gas. Although carbon formation has been widely studied from different aspects (e.g., catalytic reactions, carbon nanotube production, PAH formation, industrial-scale coking problems, and electrochemical synthesis), the variation in test conditions is immense, complicating the direct comparison of the results. Besides our own publications [27,35], the carbon formation in the reforming of tar at or above 700 °C has been studied with various nickel-containing catalysts for biomass pyrolysis volatiles [36–40], toluene model compound [37,38,41–49], phenol model compound [24,50], naphthalene model compound [24,37,40,48,49], benzene model compound [48,49] and 1-methylnaphthalene model compound [51].

During our earlier study [35], we noticed that there was a significant carbon accumulation on the nickel catalyst at 950 °C after 450 h of continuous operation, but in a parallel experiment with a noble metal catalyst, there was only a thin layer of soot on reactor walls and catalyst particles after 564 h. Since the soot was formed thermally, we were interested to find out if the noble metal catalyst promotes the removal reactions of the carbon, thereby inhibiting coke accumulation. However, the difference in the carbon formation of the nickel and noble metal catalysts is a rarely researched topic.

The reason why carbon formation is lower on noble metal catalysts than on nickel is subject to several theories. Specifically for the case of whisker carbon formation, smaller crystal sizes, which inhibit the formation of the carbon nanotube [52] and lack of carbon solubility through noble metal crystal [53], have been proposed. Theories applicable for both whisker and encapsulating carbons propose weaker carbon adsorption leading to a lack of a sufficient amount of carbon coverage to initiate the formation of graphitic rings [9,54], and the lower activity towards C–C bond formation, leading to a lack of activity towards carbon formation [41]. However, these theories are related to catalytic carbon formation and therefore do not explain the case in which thermally produced carbon deposited on catalyst surface is removed more effectively on noble metal than on the nickel catalyst.

During the reforming and carbon formation at temperatures relevant to this study (above 900 °C), the following major reactions take place in the reactor: Steam reforming of methane (1), steam reforming of higher hydrocarbons (2), water–gas–shift reaction (3), formation of carbon from methane (4) [9], formation of carbon from higher hydrocarbons (5) and (6) [9], reverse Boudouard reaction (7), and gasification reaction (8). If the higher

Figure 1. Different options for carbon formation from catalytic and thermal reactions and the resulting effect on the catalytic reactor.
hydrocarbon in reaction (6) is an aromatic hydrocarbon, the aromatic ring can also directly react to form coke instead of decomposing first to olefins.

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\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298} = 206 \text{ kJ/mol} \\
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298} > 0 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298} = -41 \text{ kJ/mol} \\
\text{CH}_4 & \leftrightarrow \text{C (s)} + 2\text{H}_2 \quad \Delta H_{298} = 75 \text{ kJ/mol} \\
\text{C}_n\text{H}_m & \rightarrow n\text{C} + 0.5 \text{mH}_2 \\
\text{C}_n\text{H}_m & \rightarrow \text{olefins} \rightarrow \text{coke} \\
\text{C (s)} + \text{CO}_2 & \leftrightarrow 2\text{CO} \quad \Delta H_{298} = 172 \text{ kJ/mol} \\
\text{C (s)} + \text{H}_2\text{O} & \leftrightarrow \text{CO} + \text{H}_2 \quad \Delta H_{298} = 131 \text{ kJ/mol}
\end{align*}
\]

The ability to avoid solid carbon formation is the key to the successful operation of any reformer designed to convert biomass gasification gas. In the worst scenario, the carbon forms slowly at first, but once the rate of carbon formation on the catalyst surface exceeds that of the carbon removal reactions (7) and (8), the carbon begins to grow at a constant rate leading to quickly to the blockage of the reactor [9,35]. The time before carbon begins to accumulate is called the induction time. Therefore, to ensure carbon-free operation, the induction time must extend over the lifetime of the catalyst in steady-state operation [9]. The feed gas composition is known to affect carbon formation, with ethylene being an especially prominent precursor compared to other hydrocarbons [9]. For example, Rostrup-Nielsen studied the effect of the H$_2$O/C molar ratio [55] and the hydrocarbon feed [56] on the induction time of nickel catalysts at 500 °C. The increasing S/C ratio prolonged the induction time, whereas the use of ethylene and benzene led to the instant formation of carbon.

In this study, the carbon formation was investigated using nickel and rhodium catalysts in a laboratory-scale reforming reaction by changing the reaction pressure, time on stream, and ethylene content in the feed gas. The studies were conducted in three separate projects that aimed for pilot-scale validation of biomass gasification and steam reforming for renewable fuel production. The gasifier types and operations varied between projects covering circulating, bubbling, and dual fluidized beds, atmospheric and pressurized operation, and oxygen addition to the gasifier. The laboratory-scale studies were adapted to best serve these projects, and therefore the test runs reported here are carried out using two slightly different feed gas compositions. Otherwise, the test conditions were chosen to replicate the operation of an industrial-scale reformer as closely as possible to provide realistic data about carbon formation.

2. Results and Discussion
2.1. Conversions and Stabilities

The main results of all experiments are summarized in Table 1. Ethylene, toluene, and naphthalene conversions were practically complete in all test runs, typical for reforming experiments with the active catalyst at high temperatures and low GHSV of 6000 l/h [6,14,35]. The conditions were similar to the pilot-scale process [5], and therefore the optimal removal of tar and light hydrocarbons was as expected. The methane and benzene conversions were only partial, with more variation due to the different test conditions. The lower conversion level of methane and benzene also allowed the detection of potential deactivation. However, it should be noted that both methane and benzene are intermediate products of the decomposition of other hydrocarbons in the reaction gas and therefore, definite conclusions can be difficult to make. For example, interesting results were obtained in the test runs 21 and 22, in which the elevated pressure led to the formation of benzene, which can be seen
in the significantly low conversion of 5% at 7 bara and even negative conversion of −6% at 10 bara.

**Table 1.** Hydrocarbon conversions and obtained carbon from test runs. Ni1 refers to commercial nickel catalyst, Ni2 to in-house nickel catalyst.

| Run | Catalyst | Variable | Conversion X (%) | $m_{\text{carbon}}$ (mg) |
|-----|----------|----------|------------------|--------------------------|
|     |          | $C_2H_4$ (vol-ppm) | $CH_4$ | $C_6H_6$ | $C_{10}H_8$ | $C_7H_8$ | $C_2H_4$ |       |
| 1   | Rh       | 0        | 50     | 94      | 100     | 100     | -       | 4     |
| 2   | Rh       | 0        | 54     | 93      | 100     | 100     | -       | 17    |
| 3   | Rh       | 5000     | 36     | 89      | 100     | 100     | 100     | 17    |
| 4   | Rh       | 10,000   | 48     | 90      | 100     | 100     | 100     | 7     |
| 5   | Rh       | 20,000   | 47     | 88      | 100     | 100     | 100     | 31    |
| 6   | Rh       | 35,000   | 55     | 90      | 100     | 100     | 100     | 45    |
| 7   | Rh       | 50,000   | 45     | 85      | 100     | 100     | 100     | 174   |
| 8   | Ni1      | 0        | 50     | 89      | 99      | 99      | -       | 31    |
| 9   | Ni1      | 5000     | 41     | 78      | 98      | 97      | 98      | 3     |
| 10  | Ni1      | 20,000   | 42     | 74      | 98      | 98      | 94      | 19    |
| 11  | Ni1      | 35,000   | 35     | 62      | 96      | 94      | 97      | 61    |
| 12  | Ni1      | 50,000   | 44     | 80      | 99      | 99      | 99      | 330   |
| 13  | Ni1      | 50,000   | 44     | 76      | 98      | 98      | 99      | 354   |
| 14  | Ni1      | 50,000   | 56     | 87      | 99      | 99      | 99      | 937   |
|     | p (bara) |          |       |         |         |         |         |       |
| 15  | Rh       | 2.5      | 68     | 100     | 100     | 100     | 100     | 60    |
| 16  | Rh       | 4        | 60     | 92      | 100     | 100     | 100     | 126   |
| 17  | Rh       | 5        | 73     | 92      | 100     | 100     | 100     | 317   |
| 18  | Rh       | 7        | 65     | 80      | 100     | 100     | 100     | 330   |
| 19  | Rh       | 10       | 54     | 76      | 100     | 100     | 100     | 384   |
| 20  | Ni1      | 4        | 61     | 79      | 99      | 100     | 98      | 195   |
| 21  | Ni1      | 7        | 50     | 5       | 96      | 100     | 89      | 150   |
| 22  | Ni1      | 10       | 58     | -6      | 94      | 100     | 92      | 69    |
|     | TOS (h)  |          |       |         |         |         |         |       |
| 23  | Ni2      | 24       | 63     | 97      | 100     | 100     | 100     | 509   |
| 24  | Ni2      | 24       | 51     | 96      | 100     | 100     | 100     | 670   |
| 25  | Ni2      | 48       | 74     | 95      | 100     | 100     | 100     | 596   |
| 26  | Ni2      | 48       | 35     | 79      | 99      | 100     | 99      | 918   |
| 27  | Ni2      | 96       | 76     | 97      | 100     | 100     | 100     | 1152  |
| 28  | Ni2      | 96       | 71     | 96      | 100     | 100     | 100     | 844   |
| 29  | Ni2      | 144      | 69     | 91      | 100     | 100     | 100     | 1448  |
| 30  | Ni2      | 144      | 65     | 96      | 100     | 100     | 100     | 1168  |
| 31  | Rh       | 144      | 35     | 84      | 100     | 100     | 100     | 39    |
| 32  | Rh       | 96       | 29     | 80      | 99      | 100     | 99      | 28    |

The operational stability of the catalysts was studied with two loadings of ethylene. The first series with 20,000 vol-ppm is depicted in Figure 2a,b for the rhodium catalyst and for nickel catalyst, respectively. Both of these runs were performed in atmospheric pressure with standard gas composition 1. In the case of methane conversion with rhodium catalyst (Figure 2a), there was a slightly decreasing trend, although it is impossible to determine if the deactivation was only a gradual loss of initial activity or resulted from sulfur poisoning or carbon accumulation. In the case of the nickel catalyst (Figure 2b), the loss of initial activity of the catalyst is very clear in methane conversion, but the activity stabilizes during the first two hours of the run, after which there is no observable deactivation.
The second series with 50,000 vol-ppm of ethylene, is depicted in Figure 3a,b for test runs 7 and 13 with the rhodium and nickel catalysts, respectively. The test conditions were otherwise fully comparable to those runs depicted in Figure 2a,b, except for the increased ethylene content and the resulting increase in carbon formation. Despite the significant carbon accumulation, the trends and conversion levels are very similar to runs with 20,000 vol-ppm of ethylene.

The long-term stability of the catalysts was studied by running two 144 h tests (Figure 4a,b), which gave similar results to the five-hour test runs (Figure 2a,b). In Figure 4a, test run 31 with rhodium catalyst shows stable and complete conversions for toluene and naphthalene. There is a clear loss of initial activity for methane during the first 12 h, which is similar to the deactivation seen during the five hours of operation (Figures 2a and 3a). After the loss of initial activity, methane conversion is fairly stable. However, benzene conversion in run 31 (Figure 4a) steadily decreases without signs of stabilization. Benzene conversion is not only affected by the ability of the catalyst to decompose it but benzene is also formed by the decomposition of toluene and reactions of ethylene. Therefore, it is difficult to determine the root cause of the drop in benzene conversion.
Figure 4. Hydrocarbon conversions as a function of operation time in (a) run 31 with rhodium catalyst and (b) run 30 with nickel catalyst. Reaction conditions: atmospheric pressure, 24,500 vol-ppm ethylene, 950 °C, TOS 144 h and gas composition 2. Ethylene is not presented, as the conversion was 100% through the test runs.

Figure 4b depicts the 144 h test run with the nickel catalyst. There is no sign of significant deactivation, although benzene conversion shows some gradual decrease that seems to have stabilized during the latter half of the experiment. Based on these examples from five and 144 h test runs on both catalysts, it is clear that the carbon did not have a significant deactivating effect on the catalyst activity.

Besides carbon formation and sulfur poisoning, it is well known that metal catalysts are susceptible to sintering at temperatures used in this study [9,23]. Sintering may also lead to catalyst deactivation, although both the catalyst composition and reaction conditions affect the sintering process [9,12]. In this study, the sintering likely began during the initial heating of the reactor in nitrogen flow. When the reaction gases entered the reactor, we also saw the immediate loss of initial activity, which typically takes place within the first few minutes of the experiment. While it is possible that the change in the chemical environment accelerates sintering at the beginning of the test run, a more likely explanation is the sulfur poisoning of the catalyst. However, long-term deactivation (such as seen in Figure 4a) could be evidence of sintering.

2.2. Effect of Ethylene on Carbon Formation

According to the literature [9,18–23], ethylene is the most reactive hydrocarbon for coke formation in typical reforming conditions and the primary precursor for the formation of PAHs. As there is always ethylene present in the biomass gasification gas, it was expected to have a significant effect on carbon formation.

The effect of increasing ethylene content from 0 to 50,000 vol-ppm with rhodium and nickel catalysts is presented in Figure 5a. It was found out that the increase of ethylene from 0 to 10,000 vol-ppm had no apparent effect on the rate of carbon formation. However, a small amount of carbon was detected in all of these test runs as carbon could also be formed from the other hydrocarbons in the feed gas, such as tars and methane. Carbon formation began to slowly increase when the ethylene content was increased to 20,000–35,000 vol-ppm, but it was only when the ethylene content reached 50,000 vol-ppm that the carbon accumulation accelerated significantly. These results indicate that as long as the ethylene level in the biomass gasification gas is below 20,000 vol-ppm, the risk for carbon accumulation in the reformer did not significantly increase.
Another important finding was that the formation of carbon was similar to the nickel and rhodium catalysts except for the highest ethylene level of 50,000 vol-ppm (Figure 5a), in which case the obtained carbon-on-nickel catalyst (test runs 12 and 13) was twice the amount on the rhodium catalyst. Furthermore, when the reaction temperature was increased with the nickel catalyst to 960 °C, the obtained carbon more than doubled again (test run 14, Table 1). In addition, the carbon accumulation increased significantly on the rhodium catalyst from 35,000 to 50,000 vol-ppm of ethylene, although the effect was not as strong as with the nickel catalyst. In the experimental conditions of this study, the carbon is formed via reactions (4)–(6), whereas reactions (7) and (8) removed carbon. The constantly accumulating carbon indicates that the catalyst had reached the point when the active sites were fully occupied with reforming and carbon removal reactions, leading to exponential carbon accumulation, similarly to what was observed by de Castro et al. [41] with toluene/methane steam reforming.

As predicted by the HSC Chemistry program (Figure 5b), the thermodynamic equilibrium composition showed a similar increasing trend of carbon formation as a function of increasing ethylene concentration, as seen in the experimental results. In addition, at the reaction temperature of 900 °C, carbon began to accumulate above the base level of around 20,000 vol-ppm of ethylene. However, contrary to our results, the thermodynamic calculation showed that a higher temperature led to lower carbon formation. In the thermodynamic equilibrium, the endothermic carbon removal reactions (7) and (8) benefited from the increased temperature, as did the reverse water–gas–shift reaction (3). Therefore, it seems that during the actual test runs, the carbon oxidation reactions were not removing carbon from the catalyst surface at the same rate as the carbon was forming. The increased temperature in the test runs only improved the rate of the thermal decomposition reaction of hydrocarbons, not that of carbon removal reactions.

Another interesting aspect of the ethylene content is its relevance as a precursor for PAHs. In our earlier study by Kaisalo et al. [14] with the same setup as was used in this study, the thermal tar formation reactions from ethylene were studied at 950 °C, which led to the formation of light components such as methane, propane, 1,3-butadiene, and acetylene, and also to the formation of aromatic compounds with 1–4 rings. In this study, the increasing ethylene concentration did not have any observable effect on the methane, ethylene, or aromatic conversions (Figures 2 and 3, Table 1). Furthermore, no indication was found by GC analysis that other light hydrocarbons or PAHs, besides those that already

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**Figure 5.** Effect of ethylene on carbon formation. (a) Carbon formation in the test runs with 0–50,000 vol-ppm of ethylene (in dry gas) with commercial nickel and rhodium catalysts. TOS 5 h. Carbon oxidized at 850 °C after the test runs. (b) Thermodynamic calculation by HSC Chemistry of carbon formation as a function of ethylene concentration in different reaction temperatures and atmospheric pressure.
2.3. Effect of Reaction Time on Carbon Formation

We ran eight separate test runs with an in-house nickel catalyst and Gas2 over an increasing TOS up to 144 h and always started with a fresh catalyst. As a comparison, two test runs with commercial rhodium catalyst were carried out for 96 and 144 h. This setup was supplemented by 5 h test runs with the rhodium and nickel using Gas1. The results in Figure 6 show that the carbon accumulation increased linearly as a function of TOS with the nickel catalyst. There was no sign of an induction time before carbon began to accumulate.

Contrary to the nickel catalyst, in the three experiments with the rhodium catalyst, the carbon formation was minor and did not increase when the TOS was increased from 5 to 144 h (Figure 6). This is an interesting result when compared to the results with increasing ethylene content (Section 2.2), in which the nickel and rhodium catalysts had similar carbon accumulation up to 20,000 vol-ppm of ethylene. If the run time of the ethylene experiments had been increased to extend the 5 h period, differences between the nickel and rhodium catalysts might have been more pronounced. In any case, it is clear that the catalyst has a significant effect on the length of the induction time and thereby on the total accumulation of carbon, as was also seen in our previous study [35].

As discussed in the introduction of this paper, the reason why the carbon accumulation on noble metal catalysts is lower than on the nickel catalyst is not fully understood. A weak bonding of carbon on the active sites has been proposed by [9,54], which might explain the easier removal of carbon from the surface of rhodium compared to that of nickel. Furthermore, a lower activity towards C–C bond formation has been proposed [41] that would inhibit the progression of carbon formation on the noble metal surface but does not explain the removal of thermally formed carbon. The fact that the amount of carbon did not increase on the rhodium catalyst between 5 h and 144 h (Figure 6) supports the theory of carbon removal reactions being in balance with the rate of both catalytic carbon formation and carbon deposition from the thermal formation.

Looking at the catalysts after each test run, Figure 7 also shows the clear difference between the nickel and rhodium catalysts. The pictures were taken from the reactor’s top-view before the carbon oxidation. These photos clearly show why carbon control is

Figure 6. Effect of reaction time on carbon formation for nickel and rhodium catalysts. The first 5 h point is with Gas1 for both catalysts; the other points with Gas2. Reaction conditions for 5 h points: atmospheric pressure, 900 °C, 20,000 vol-ppm ethylene and gas composition 1. Reaction conditions for 24–144 h points: atmospheric pressure, 950 °C, 24,500 vol-ppm ethylene and gas composition 2.
important, as the top layer of the catalyst bed can be fully covered by carbon and in some pictures (for example, runs 27–30), there are clear signs of solid formations that would eventually block the entire reactor. The majority of the carbon was located in all test runs to this topmost layer of the catalyst bed and on the reactor walls above it, which verifies that the carbon was at least partially formed thermally. As we were aiming to compare total carbon amounts from each test run, it was impossible to take samples from different positions in the catalyst bed for carbon analysis. However, despite a high accumulation of carbon, a build-up of pressure drop was not observed during any of these test runs. In our previous study, the total blockage of the reactor required only 150 h of continuous operation [35], and in that case, the pressure drop increased exponentially only during the final hour before the automatic safety shutdown. As the catalyst conversions were not affected either, there was no outward sign of carbon accumulation, which underlines the importance of increasing the understanding of the carbon formation in the reforming of tar-laden gases.

![Figure 7. Top view of the reactor after each TOS test run with nickel and rhodium catalysts.](image)

2.4. Effect of Pressure on Carbon Formation

The effect of increasing reaction pressure is not usually considered in the reforming studies as it shifts the balance of reaction (1) back towards methane. However, in the case of biofuel production via gasification and Fischer–Tropsch synthesis, the elevated pressure can be beneficial for the economics of the entire process, and therefore also reforming unit could be pressurized [14]. The effect of increased pressure in the test runs with nickel and rhodium catalysts is presented in Figure 8a for carbon formation and Figure 8b for hydrocarbon conversions. Based on the thermodynamic calculation (Figure 8c), it was expected that the carbon accumulation would begin above 3 bar pressure and then increase as a function of pressure. In the test runs (Figure 8a), the rhodium catalyst was found to roughly follow the thermodynamic model, but on the nickel catalyst, the increase of pressure to 7 bar and to 10 bar suppressed the formation of carbon.

The effect of pressure on carbon formation is a complex topic. Using Le Chatelier’s principle, we can hypothesize that carbon formation reactions (4) and (5) are suppressed in increased pressure as they form gaseous hydrogen besides solid carbon. The carbon removal reactions (7) and (8) should also be suppressed or even progressed in the reverse direction, i.e., towards coke formation. However, the olefin route from ethylene and tars (6) should be promoted, as was seen in the study by Kaisalo et al. [14], where the increase of pressure in the thermal formation of PAHs from ethylene increased the conversion towards heavier PAHs. Furthermore, the increased pressure leads to increased residence time, which can be expected to favor at least the production of thermal carbon.
Figure 8. Effect of pressure on (a) carbon formation and (b) CH₄, C₂H₄, C₆H₆ and C₁₀H₈ conversions for Ni- and Rh-catalysts (test runs 5, 10, 15–22). Reaction conditions: pressure 1–10 bara, 20,000 vol-ppm ethylene, 900 °C, TOS 5 h and gas composition 1. (c) Carbon formation according to thermodynamic calculation by HSC Chemistry.

The primary question concerns the effect of pressure on the activity of nickel and noble metal catalysts for both carbon formation and carbon removal reactions. In studies [57–59] on the decomposition of methane for the purposeful production of carbon nanotubes, the effect of pressure in the range of atmospheric to 10 bar was investigated on a nickel catalyst. The major conclusion was that the initial carbon formation rate decreased with the increasing pressure due to increased coverage of hydrogen on active sites, inhibiting the nucleation of graphitic carbon. However, this inhibiting effect led to an increased lifetime of the catalyst and thereby increased the total production of carbon over the total TOS. This type of pressure-dependent change in catalyst activity would be the most probable explanation for the behavior seen for the nickel catalyst in our experiments (Figure 8a).

Considering the carbon formation and removal reactions (4), (5), (7) and (8), an interesting question is raised about the source for the accumulated carbon on the nickel and rhodium catalysts in this study. The HSC Chemistry simulation for reactions (4), (7) and (8) in Figure 9 shows that the carbon formation via a Boudouard reaction (reverse reaction (7)) and the reverse gasification reaction (reverse reaction (8)) is promoted by the increasing pressure. However, Figure 9 also shows that in the conditions relevant to our study (900 °C and 1–10 bar), a Boudouard reaction did not lead to carbon formation. On the other hand, the methane decomposition reaction (4) was suppressed by the increasing pressure.
Considering the carbon formation and removal reactions (4, 5, 7 and 8), an interesting question is raised about the source for the accumulated carbon on the nickel and rhodium catalysts in this study. The HSC Chemistry simulation for reactions (4), (7) and (8) in Figure 8b showed that the methane decomposition reaction (4) was suppressed by the increasing pressure. However, Figure 9 also shows that in the conditions relevant to our study (900 °C and 10 bar), the reverse gasification reaction (reverse reaction 8) is promoted by the increasing pressure. It is also possible that the carbon adsorption to the active sites of rhodium was strengthened by the increased pressure, or the carbon formation on the rhodium catalyst has been inhibited by weak adsorption of carbon atoms to active sites [9,54] or by a lack of activity toward C—C bond formation [41]. If the increasing pressure also increases the adsorption of hydrogen on the rhodium catalyst (as it is expected to do with nickel catalyst), it would lead to the competition of active sites between hydrogen and carbon removal reactions. Furthermore, according to the literature, the carbon formation on the rhodium catalyst was promoted by pressure, which would explain both the difference between the nickel catalyst and the rhodium catalyst in atmospheric conditions. However, when the pressure is increased, the combined effect of hydrogen blocking of the active sites and lower thermodynamic potential towards hydrocarbon decomposition, led to a drop in carbon formation. This assumption is also supported by the significant decrease in benzene conversion down to −6% at 10 bar and a milder reduction in ethylene and naphthalene conversions (Table 1), which are direct consequences of decreased activity towards hydrocarbon decomposition (Figure 8b).

As discussed earlier, the low carbon formation on the rhodium catalyst in the time-on-stream experiments (Section 2.3) indicated that the rhodium catalyst promoted carbon removal reactions. Furthermore, according to the literature, the carbon formation on the rhodium catalyst has been inhibited by weak adsorption of carbon atoms to active sites [9,54] or by a lack of activity toward C—C bond formation [41]. If the increasing pressure also increases the adsorption of hydrogen on the rhodium catalyst (as it is expected to do with nickel catalyst), it would lead to the competition of active sites between hydrogen and carbon removal reactions. It is also possible that the carbon adsorption to the active sites of rhodium was strengthened by the increased pressure, or the carbon formation on the rhodium catalyst was promoted by pressure, which would explain both the difference between the nickel catalyst and the carbon accumulation seen in Figure 8a.

### 2.5. Carbon Characterization

Total carbon accumulation was measured after each test run by three different methods. In all experiments, the carbon was oxidized in situ, and the quantitative calculation was based on CO and CO₂ analysis by a continuous gas analyzer. Secondly, oxidation after run 14 was done in situ using the TPO method and FTIR for a detailed analysis of carbon oxidation (Figure 10). Thirdly, the reactors from test runs 23–32 were removed from the setup and visually inspected before installing them again to the setup for the oxidation (Figure 7). No samples were taken from the carbon for ex situ analysis as it would have affected the quantitative analysis.

![Figure 9. The effect of pressure and temperature on carbon formation from methane decomposition (4), from CO (reverse Boudouard reaction, (7)), and from CO and H₂ (reverse gasification reaction, (8)). HSC calculation is based on thermodynamic equilibrium. Carbon content in feed set to 1 mol.](image-url)
The formation of whisker carbon (a.k.a. carbon nanotubes, carbon filaments) was not expected in this study as this form of carbon is inhibited by the H2S as indicated by the literature [9] and our previous studies [27,35]. The nucleation of the first graphitic ring for the whisker is determined to require 6–7 carbon atoms adsorbed on adjacent sites [60], which is incidentally why partial blocking of the sites by sulfur inhibits the formation of the whisker carbon [9,27]. However, the whisker carbon often appears in the literature when tar model compounds are tested for steam reforming. The reason for this difference is that the feed gases in these studies are sulphur-free.

The formation of whisker carbon is easily observable as the visible destruction of the catalyst particles, and therefore whisker carbon is easy to distinguish from the encapsulating carbon after the experiments. Unlike the encapsulating carbon, whisker carbon does not lead to immediate deactivation as, despite the structural destruction of the catalyst, the nickel crystal remains accessible to the reaction gas [9]. As discussed in Section 2.1, the steam reforming reactions in our studies were not affected even though carbon was accumulating in increasing amounts on the front face of the catalyst bed (as seen in Figure 7). The potential deactivating effect of the encapsulating carbon was therefore only localized to the topmost part of the catalyst bed, while the catalyst particles beneath were not affected and were capable of maintaining the overall steam reforming activity of the reactor. Therefore, deactivation could not be used to determine whether the type of the carbon was whisker or encapsulating. In our earlier studies [27], the appearance of whisker carbon led to the immediate and complete destruction of the catalyst particles. To verify the lack of whisker carbon formation in this present study, we inspected all catalyst particles after oxidation and found no signs of breakdown caused by whisker growth, as can be seen in the example in Figure 11.

In the conditions relevant to this study (i.e., 900 °C and H2S in the feed gas), the appearance of encapsulating atomic, amorphous and graphitic carbon was expected. The oxidation of different forms of carbon takes place at different temperatures, depending on how easy they are to oxidize. In Figure 10, the TPO reveals CO2 peaks at ca. 430 °C, 600 °C, 830 °C and 890 °C oxidation temperatures. There was also a corresponding temperature increase in the reactor at 430 °C and 830 °C due to an exothermic combustion reaction. These peaks are assigned in the literature [15,27,28,42,61–65] for easily oxidizing carbon atoms or short carbon chains below 500 °C, amorphous carbon and whisker carbon around

Figure 10. Oxidation by TPO method in run 14. Analysis of CO and CO2 in outlet gas by FTIR and gas analyzer as a function of time from the beginning of the oxidation. Temperature measurement inside the reactor shows the corresponding peaks to major CO2 peaks.
500–700 °C and graphitic encapsulating carbon at and above 700 °C. Figure 10 would therefore indicate that most of the carbon formed in run 14 was graphitic. As the peaks for atomic and amorphous carbon are very small compared to the peak of graphitic carbon, it can be assumed that the conditions have been beneficial for the immediate progress of the carbon formation reaction toward graphitic rings.

The comparison of the oxidation results with literature is not straightforward as in practically all relevant literature the feed gas lacks H2S. In those tar model compound studies in which the type of carbon was analyzed, whisker carbon was typically identified along with amorphous carbon but no encapsulating carbon was observed [24,42,44,45,48–51]. Other studies [43,46] used analysis methods (mainly Raman) to differentiate amorphous and graphitic carbon, but it was not disclosed whether the graphitic carbon was identified as whisker or encapsulating carbon. As none of these studies included H2S in the feed gas, the primary form of whisker carbon was as expected but does not offer comparable data for our research. In the study by de Castro et al. [41] with the noble metal catalyst at 700 °C, whisker carbon was not found (as it does not form on noble metals). Still, the Raman analysis of the coke indicated a higher proportion of amorphous carbon compared to graphitic carbon, which would suggest that the formed encapsulating carbon had a relatively high amount of non-aromatic structures.

Finally, our earlier studies about carbon formation [27,28] showed that the TPO peak for the whisker and amorphous carbon on the nickel catalyst always appeared around 500–700 °C. Often a second peak or a shoulder peak was found above 700 °C, indicating the presence of more highly structured graphitic carbon. As there was no other evidence of whisker carbon in our present experiments, it can be concluded that the carbon oxidized in Figure 10 was primarily encapsulating, highly structured graphitic carbon.

3. Materials and Methods

3.1. Catalysts

Three catalysts were used in the test runs: an in-house 13 wt% Ni/Al2O3 catalyst, a commercial calcium doped 14–15 wt% NiO/Al2O3 and a commercial noble metal catalyst, with rhodium as its main active component and alumina as support material. The commercial catalysts were 3 mm particles of the same catalysts used in the pilot-scale test runs and within confidentiality agreements. The in-house Ni/Al2O3 was prepared by the incipient wetness impregnation method. Nickel (II) nitrate hexahydrate Ni(NO3)2·6H2O (purum p.a. crystallized ≥ 97.0%, 72253, Sigma-Aldrich, St. Louis, MO, USA) was used as the precursor. The precursor was diluted with ion-exchanged water. The support (x-alumina SA 51131, 3 mm pellets, Saint-Gobain NorPro, Stow, OH, USA) was dried under a vacuum of 50 mbar and a temperature of 150 °C for two hours. Then the support was cooled down and the vacuum decreased down to 10 mbar. The precursor solution was impregnated on the alumina support and left overnight to settle. The wet catalyst was again dried in
a rotary evaporator at 80 °C until a vacuum of 10 mbar was reached. The dry catalytic particles were then calcined at 500 °C for two hours.

3.2. Experimental Setup

The experiments were carried out in a pressurized plug flow reactor setup, depicted in Figure 12. It can feed several fixed-line gases and add steam and model tar to the gas mixture to replicate the biomass gasification gas as closely as possible. The gases used in the experiment were obtained from AGA, and their purities were N₂ 99.999%, H₂ 99.999%, CH₄ 99.5%, CO 99.97%, CO₂ 99.99% C₂H₄ 99.95% NH₃ 5 mol% in N₂, H₂S 0.005% in N₂ and O₂ 99.999%. The model tar compound contained 10 wt% naphthalene (Merck >99%), 10 wt% benzene (Merck 99.7%) and 80 wt% toluene (Merck 99.9%). The gas compositions are given in Table 2.

![Figure 12. Plug flow reactor used in the carbon formation studies.](image)

Table 2. Gas composition for the carbon formation experiments. Gas1 [66] and Gas2 [5,67] refer to two different types of biomass gasification gas compositions used in this study.

| Gas | CO  (vol%) | CO₂  (vol%) | H₂  (vol%) | CH₄  (vol%) | O₂  (vol%) | N₂  (vol%) | C₂H₄  (vol%) | H₂O  (vol%) | NH₃  (vol-ppm) | H₂S  (vol-ppm) | Tar  (vol-ppm) |
|-----|-----------|------------|-----------|------------|-----------|-----------|-------------|-----------|----------------|----------------|---------------|
| 1   | 14.9      | 11.9       | 20.9      | 6          | 0         | 4.7       | 1.2         | 40        | 1200           | 60             | 2900          |
| 2²  | 7.2       | 18.7       | 21.6      | 5          | 2         | 3.4       | 1.5         | 40        | 1200           | 60             | 4400          |

¹ In those experiments where ethylene was changed, the variation was from 0 to 50,000 vol-ppm in dry gas. The N₂ content was changed accordingly. ² The fuel-to-oxygen ratio of Gas2 was 9.1.

The catalyst was packed inside a quartz reactor tube on a sinter (Figure 13). Before the test run, the reactor containing the catalyst was inserted into the furnace, and the entire system was purged with nitrogen to remove any traces of air. The reactor was pressure-tested for leakages and once everything was satisfactory, the reactor was heated to the experiment temperature. The heating was done with a three-zone electric furnace. In experiments 23–32, a minor part of the heating was also produced by introducing 2 vol% of oxygen into the feed gas. Once the reactor was at the correct temperature, the nitrogen flow was turned to the bypass line. The reactive gas components were added, and the inlet gas composition was measured by GC and a gas analyzer. When the inlet gas composition was stable, the gas was turned into the reactor. The reaction gas reduced the catalyst instead of a separate H₂/N₂ treatment. This is a standard method in our reforming tests with gasification gas and verified in earlier studies [12,68]. The operating conditions of each test...
run are given in Table 3. The flow rate in all test runs was 2 L\textsubscript{m}/min leading to GHSV of circa 6000 1/h. The length of each experiment varied from 5 h to 144 h.

![Catalysts in reactors before the experiments. (a) Rhodium; (b) nickel. A thermoelement pocket runs through the catalyst bed.](image)

**Table 3.** Operating conditions of each test run. Ni1 refers to commercial nickel catalyst, Ni2 to in-house nickel catalyst.

| Run | Catalyst | Feed Gas | \(m_{\text{catalyst}}\) (g) | \(p\) (bara) | \(T\) (\(^{\circ}\)C) | \(\tau\) (s) | TOS (h) | S/C Molar | \(\text{C}_2\text{H}_4\) (vol-ppm, Dry Gas) |
|-----|----------|----------|----------------|-----------|----------------|-----------|--------|----------|----------------|
| 1   | Rh       | Gas1     | 22.0           | 1         | 900            | 0.07      | 5      | 6.4      | 0              |
| 2   | Rh       | Gas1     | 22.6           | 1         | 900            | 0.07      | 5      | 6.4      | 0              |
| 3   | Rh       | Gas1     | 22.6           | 1         | 900            | 0.07      | 5      | 5.8      | 10,000         |
| 4   | Rh       | Gas1     | 22.6           | 1         | 900            | 0.07      | 5      | 5.4      | 20,000         |
| 5   | Rh       | Gas1     | 22.6           | 1         | 900            | 0.07      | 5      | 4.8      | 35,000         |
| 6   | Rh       | Gas1     | 22.5           | 1         | 900            | 0.07      | 5      | 4.3      | 50,000         |
| 7   | Rh       | Gas1     | 22.6           | 1         | 900            | 0.07      | 5      | 4.3      | 50,000         |
| 8   | Ni1      | Gas1     | 22.9           | 1         | 900            | 0.07      | 5      | 6.4      | 0              |
| 9   | Ni1      | Gas1     | 21.6           | 1         | 900            | 0.07      | 5      | 6.1      | 5000           |
| 10  | Ni1      | Gas1     | 21.6           | 1         | 900            | 0.07      | 5      | 5.4      | 20,000         |
| 11  | Ni1      | Gas1     | 21.6           | 1         | 900            | 0.07      | 5      | 4.8      | 35,000         |
| 12  | Ni1      | Gas1     | 21.6           | 1         | 900            | 0.07      | 5      | 4.3      | 50,000         |
| 13  | Ni1      | Gas1     | 22.9           | 1         | 900            | 0.07      | 5      | 4.3      | 50,000         |
| 14  | Ni1      | Gas1     | 22.9           | 1         | 900            | 0.07      | 5      | 4.3      | 50,000         |
| 15  | Rh       | Gas1     | 22.6           | 2.5       | 900            | 0.17      | 5      | 5.4      | 20,000         |
| 16  | Rh       | Gas1     | 22.6           | 4         | 900            | 0.27      | 5      | 5.4      | 20,000         |
| 17  | Rh       | Gas1     | 22.6           | 5         | 900            | 0.34      | 5      | 5.4      | 20,000         |
| 18  | Rh       | Gas1     | 22.6           | 7         | 900            | 0.48      | 5      | 5.4      | 20,000         |
| 19  | Rh       | Gas1     | 22.6           | 10        | 900            | 0.68      | 5      | 5.4      | 20,000         |
| 20  | Ni1      | Gas1     | 21.6           | 4         | 900            | 0.27      | 5      | 5.4      | 20,000         |
| 21  | Ni1      | Gas1     | 21.5           | 7         | 900            | 0.48      | 5      | 5.4      | 20000          |
| 22  | Ni1      | Gas1     | 21.6           | 10        | 900            | 0.68      | 5      | 5.4      | 20,000         |
| 23  | Ni2      | Gas2     | 25.0           | 1         | 950            | 0.06      | 24     | 3.6      | 24,500         |
| 24  | Ni2      | Gas2     | 25.1           | 1         | 950            | 0.06      | 24     | 3.6      | 24,500         |
| 25  | Ni2      | Gas2     | 25.1           | 1         | 950            | 0.06      | 48     | 3.6      | 24,500         |
| 26  | Ni2      | Gas2     | 25.0           | 1         | 950            | 0.06      | 48     | 3.6      | 24,500         |
| 27  | Ni2      | Gas2     | 25.0           | 1         | 950            | 0.06      | 48     | 3.6      | 24,500         |
| 28  | Ni2      | Gas2     | 25.0           | 1         | 950            | 0.06      | 48     | 3.6      | 24,500         |
| 29  | Ni2      | Gas2     | 25.0           | 1         | 950            | 0.06      | 48     | 3.6      | 24,500         |
| 30  | Ni2      | Gas2     | 25.0           | 1         | 950            | 0.06      | 48     | 3.6      | 24,500         |
| 31  | Rh       | Gas2     | 22.8           | 1         | 950            | 0.06      | 144    | 3.6      | 24,500         |
| 32  | Rh       | Gas2     | 24.1           | 1         | 950            | 0.06      | 144    | 3.6      | 24,500         |
The reactor temperature was measured during the test runs by a K-type thermocouple that was placed inside the catalyst bed within a quartz thermocouple pocket. Similarly, the pressure drop across the reactor was monitored throughout the experiments to detect any signs of pressure increase due to reactor blockage by carbon formation.

3.3. Gas Analysis System

The downstream part of the reactor setup was designed to allow multiple online measurements. First, the hydrocarbons of the outlet gas were analysed by an Agilent 7890A gas chromatograph, which was working online throughout the test run and equipped with one injector, two flame ionization detectors (FID), and three columns that were Agilent GS-GASPRO (30 m × 0.32 mm ID, 0 µM film), HP-5 (30 m × 0.32 mm ID, 0.25 µM film) and a restrictor column (3 m × 0.18 mm). The gas was led through a heated line to a 0.25 mL sample loop in a six-port valve through the injector to the HP-5 column. Before benzene and heavier hydrocarbons were eluted from the HP-5-column the gas flow direction was changed by a Deans switch system to send lighter hydrocarbons to GS-GASPRO-column. Heavier hydrocarbons continued to the detector through a restrictor column. The carrier gas was helium. The initial temperature was 100 °C. An oven program 100 °C-9.2 min-20 °C/min-250 °C-12.3 min was set to the gas chromatograph, and the total run time was 30 min. The chromatograph was calibrated with different light calibration gas mixtures and with the feeding gas through the bypass line.

After the GC sample line, the product gas was dried by condensing all components that are in a liquid state at room temperature, i.e., water and tar components. The flow rate of the dry gas was then measured, and the gas composition was analyzed continuously by an online SICK Maihak S710 gas analyzer. H₂ was measured by a thermal conductive detector (TCD), CO, CO₂ and CH₄ were measured by non-dispersive infrared adsorption (NDIR), and O₂ was measured by an oxygen cell. A SICK Maihak analyzer was calibrated with a calibration gas mixture.

3.4. Carbon Oxidation

After each experiment, the carbon was oxidized using a gas mixture of O₂/N₂ 15/85 vol% (runs 1–22) or 20/80 vol% (runs 23–32), a flow rate of 2 L/min and a temperature of 850–900 °C. The differences in the oxidation conditions were not expected to have an effect on the results. In test run 14, the carbon measurement was carried out as a temperature-programmed oxidation (TPO) in which the reactor is slowly heated during oxidation. This method provides an opportunity to analyze if there are different forms of carbon that oxidize at different temperatures. For this analysis, using a Fourier Transform Infrared Spectrometer (FTIR, Gasmet9540) was necessary, as it could detect far smaller CO and CO₂ peaks than the gas analyzer. Unfortunately, FTIR was only available for this specific run, and therefore all other experiments were carried out as normal oxidations instead of TPO.

The full contents of the reactors were oxidized without taking any samples for other analysis. The pyrolytic carbon that was formed during the experiments, appears both on the top of the catalyst bed and on the inside walls of the reactor. Therefore, it was impossible to take a representative sample of the carbon. In addition, as the primary objective of these test runs was to quantitatively analyze the carbon formed at different reaction conditions, sampling would have led to material losses and affected the reliability of the results. Therefore, no other analysis was performed on the carbon except the oxidation.

3.5. Calculation Methods

The conversions and steam to carbon (S/C) molar ratios were calculated using gas analysis data and dry gas flow measurements. The amount of carbon was calculated from CO and CO₂ peaks in the gas analyzer during oxidation. The S/C molar ratio included all feed gas hydrocarbons.
The conversion $X_i$ was calculated by using Equation (9). The calculation was based on the molar flow $\dot{n}$ of component $i$ in and out of the system. Ideal gas law assumption was used in the calculations.

$$X_i(\%) = \frac{\dot{n}_{i,IN} - \dot{n}_{i,OUT}}{\dot{n}_{i,IN}} \cdot 100\%$$  \hspace{1cm} (9)

The S/C molar ratio was calculated by using Equation (10) and the molar flow $\dot{n}$ of water, methane, ethylene, benzene, toluene and naphthalene.

$$\frac{S}{C} = \frac{\dot{n}_{H_2O}}{\dot{n}_{CH_4} + \dot{n}_{C_2H_4} + \dot{n}_{C_6H_6} + \dot{n}_{C_7H_8} + \dot{n}_{C_{10}H_8}}$$  \hspace{1cm} (10)

Outotec HSC version 9.0.7 software was used for the thermodynamic equilibrium calculations. HSC calculation was based on the minimization of Gibbs free energy for a given gas composition at a given temperature and pressure. The thermodynamic data for all components were obtained from the HSC database, and graphite data was used to represent solid carbon. The effects of increasing ethylene concentration and increasing pressure on carbon formation were analyzed. As the HSC calculates the product composition at the thermodynamic equilibrium, even small amounts of water in the feed gas inhibit the formation of solid carbon. Therefore, the water was replaced by inert nitrogen in the feed gas to simulate a situation in which the carbon oxidation reactions could not progress and carbon formation starts.

4. Conclusions

Based on the results and reviewed literature, we conclude that the most likely explanation for the different behaviors of the catalysts is that in atmospheric conditions, the nickel catalyst promoted carbon formation, whereas the rhodium catalyst promoted carbon oxidation, leading to lower carbon formation on the rhodium catalyst. Elevated pressure was known to increase the thermal formation of PAHs and coke. In these studies, pressure deactivated the catalytic carbon formation reaction on the nickel catalyst and increased the activity towards the carbon removal. However, on the rhodium catalyst, pressure increase led to higher carbon formation, possibly due to deactivated carbon oxidation reaction or promoted reaction of carbon formation.

To summarize the characterization of the carbon, no evidence of whisker carbon formation was found. Instead, the carbon formed in our test conditions was characterized as encapsulating carbon. The amount of graphitic content appeared to be high compared to amorphous, although it could not be verified by multiple analyses.

To avoid carbon formation in the reforming of biomass gasification gas, atmospheric conditions and a low ethylene content below 20,000 vol-ppm were found to be preferable. The use of noble metal catalysts should be carefully considered, at least for initial tar removal, as they can offer a significant advantage in long-term operations compared to the nickel catalyst.

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