Article

Performance of Catalysts of Different Nature in Model Tar Component Decomposition

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Abstract: Municipal solid waste constitutes one of the major challenges and concerns of our society. Disposal of waste material is potentially dangerous, harming both environment and mankind. In order to diminish negative effects of municipal solid waste, its thermal decomposition to valuable chemicals has been studied. The principal draw-back of thermal processes used for solid waste utilization as raw material is tar formation. In this study, low-cost catalysts of different origin were tested in the decomposition of a model component of tar originating from waste material pyrolysis/gasification. p-Xylene was selected as the model compound found in biomass decomposition products. Its decomposition was carried out in the presence of either tire pyrolysis char- or clay minerals-based catalysts. Tar-cracking activities of both catalyst types at varying experimental conditions were compared and related to the catalysts physical-chemical properties. In experiments, either empty reactor or reactor filled with 10 g of the catalyst was used; p-xylene mass flow was set to 2.58 g h⁻¹ (50 µL min⁻¹, room temperature), and decomposition temperature ranging from 750 °C to 850 °C was applied. Moreover, evolution of the output variables, p-xylene conversion and hydrogen content in the gas phase, with the reaction time was investigated. Catalysts’ properties were assessed based on nitrogen adsorption isotherms, thermogravimetric and elemental composition analyses. Amounts and composition of p-xylene catalytic decomposition products were evaluated using GC analysis of both gaseous phase and condensable products. Results showed the superiority of tire pyrolysis char catalyst over that based on clay minerals.

Keywords: biomass thermal treatment; gasification; tar catalytic decomposition; tire pyrolysis char; clay minerals

1. Introduction

Municipal solid waste (MSW) production has become an important issue recently. According to The World Bank, up to 2.01 billion tons of MSW were generated worldwide in 2016, which corresponds to 0.74 kg of waste per person and per day [1]. Projection of its production rate yields 3.40 billion tons of MSW in 2050. Disposal of waste material in landfills and dumps is dangerous, threatening the environment and humanity itself; still, these are the most frequently used strategies of MSW treatment. Globally, about 37% of waste is landfilled and 33% of it is disposed of via open dumping [1]. In order to mitigate negative effects of MSW “storage”, two main policies should be adopted, minimization of waste production and waste recycling. To do so, MSW has to be considered as a valuable product and, at the same time, valuable source of energy and raw materials.

Energetic and material recycling of MSW, however, requires the development of treatment processes. Due to the diversity of materials forming municipal solid waste, separation of MSW
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constituents should precede its recycling and recovery. For this purpose, mechanical–biological
treatment (MBT) of MSW can be used. During MBT, organic (food waste, compostable biomass) and
inorganic (construction materials, glass, metal particles) waste fractions of MSW are separated from
recyclable materials denoted as refuse-derived fuel [2]. Main components of refuse-derived fuel (RDF)
are paper, cardboard, plastic, textile and wood. The amount of RDF corresponds to approximately 40%
of the original mass of MSW [3] representing a substantial amount of the MSW energy content.

One of the possibilities of RDF conversion to valuable chemicals and energy is its gasification or a
combination of RDF gasification with pyrolysis. In case of waste material recycling, process gas is the
desired product of RDF gasification. Process gas contains mainly methane, carbon oxides, hydrogen,
nitrogen and water vapor [4,5]. Further RDF gasification products are char and tar. Composition
of these products (process gas, tar and char) is affected not only by the composition of RDF and the
oxidation agent used but also by the conditions in the gasification reactor and by the reactor design [6,7].
Principal draw-back of RDF gasification aimed at the production of process gas as feed stock for a
chemical plant or a source of energy is the formation of tar, the presence of which leads to laborious
down-stream processing of process gas prior to its final use. Tar is a mixture of condensable compounds
formed in a gasification reactor via thermal decomposition of RDF in sub-stoichiometric conditions
with regard to RDF oxidation. Although there is no general definition of tar, it is commonly accepted
that compounds with higher molecular mass than benzene belong to this class of components [7,8].

At elevated temperatures in the gasification reactor, tar components are present in the gaseous
phase; however, a decrease in temperature leads to their condensation. In condensed phase, tar
components form dark brown viscous liquid sticking to colder inner surfaces of the equipment cause
its obstruction and malfunction [5].

In order to separate condensables from process gas, either physical or chemical methods are
applied [7]. Physical methods of tar removal can be classified according to temperature applied in the
separation units represented by cyclones, filters, absorbers, etc. [9]. Efficiency of physical tar-trapping
methods is constantly increasing. Recently, up to 90% tar separation from process gas was reported for a
mop fan coupled with a water spraying system used for tar capture [10]. Chemical abatement of tar, its
cracking/decomposition/conversion, is carried out either in a separate reactor (ex situ) or directly in the
gasification reactor (in situ). Processes of tar thermal decomposition and catalytic conversion to lower
molecular mass compounds are applicable and show some advantages as well as shortcomings. In case
of tar thermal decomposition, temperatures exceeding 800 °C are required. Moreover, this process is
accompanied by poly-aromatic hydrocarbons and soot formation [7,11]. On the other hand, the use of
catalysts makes tar decomposition more complex. The catalyst enhances tar cracking; however, it can
be a subject of deactivation due to the presence of catalytic poisons such as sulfur, chlorine and trace
metals in process gas and tar. A short review of catalysts with potential in tar cracking can be found in
a monography by Schildhauer and Biollaz [12]. Among these materials, natural clays and catalytic
char are listed for their good to very good activity and low price. Tar cracking activity of catalysts and
hydrogen content in the resulting process gas can be further increased by an addition of nickel [13] or a
combination of nickel and iron [14,15].

In the present study, catalytic activity of Ni-doped clay mineral and tire pyrolysis char catalysts
was tested in the decomposition of a model tar component, \( p \)-xylene. Composition of the treated
gaseous phase was analyzed with regard to permanent as well as condensable reaction products. The
effect of reaction time on the product composition was also investigated. Catalyst structure–activity
relationship was elucidated based on the results of standard solid material characterization techniques,
such as adsorption of nitrogen and TG analysis.
2. Results and Discussion

2.1. Catalysts Characterization

Composition of calcined clay mineral determined by X-ray fluorescence analysis is presented in Table 1. These data were originally given in our previous paper [16]. Results of X-ray diffraction analysis of this clay material showed the presence of annite, quartz, lime, hematite and periclase. In Table 1 also elemental analysis of carbonized (activated) pyrolysis char is given. Oxygen content was deduced from the difference between the sample mass and the mass of the other reported char components. The amount of ash was determined based on TG analysis of the char sample. Metals content in the pyrolysis char catalyst can be found in our previous study [17].

Table 1. Clay mineral chemical composition [16] and pyrolysis char elemental composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Clay Mineral</th>
<th>Pyrolysis Char</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>w [mass%]</td>
<td>63.16 ± 0.14</td>
<td>8.89 ± 0.02</td>
</tr>
<tr>
<td>Element</td>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>w [mass%]</td>
<td>72.91 ± 0.64</td>
<td>2.47 ± 0.03</td>
</tr>
</tbody>
</table>

Almost all components of natural clay tested in this study are active in tar decomposition [12]. Comparing calcined catalysts, tar-cracking activity of SiO₂, Al₂O₃ and iron oxides in clay minerals is lower than that of dolomite principal component (CaO). On the other hand, clay thermal stability and attrition resistance at conditions in the catalytic tar decomposition reactor are slightly higher compared to those of dolomite. Further increase of clay mineral activity in the tar-cracking reaction can be achieved doping them with transition metals of the iron group. Activity in this reaction and selectivity towards hydrogen was ascribed to nickel oxide and metallic nickel supported on diverse support materials such as alumina [18], olivine [19] or dolomite [13].

Pyrolysis char activity in the tar-cracking reaction dwells in its high specific surface area that is, at the same time, responsible for its high adsorption ability [12]. High content of ash in tire pyrolysis char (Table 1) corresponds to additives (ZnO, etc.) that may further improve its catalytic activity. On the other hand, the presence of sulfur may cause pollution of product gas with volatile sulfur compounds, although char is considered to be an excellent adsorbent for these contaminants [12].

Nitrogen adsorption results are presented in Table 2. Standard BET adsorption isotherm procedure was used to calculate the catalysts specific surface area. Specific pore volume and average pore diameters of the investigated catalysts were estimated based on the BJH method. Data for Ni-doped clay mineral catalyst were originally published in our previous study [16].

Table 2. Results of N₂ adsorption on Ni-doped (3 mass%) clay mineral [16] and carbonized pyrolysis char catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_BET [m² g⁻¹]</th>
<th>v_p [cm³ g⁻¹]</th>
<th>d_p [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-doped clay</td>
<td>28.6</td>
<td>0.17</td>
<td>7.8</td>
</tr>
<tr>
<td>Pyrolysis char</td>
<td>67.5</td>
<td>0.32</td>
<td>17.4</td>
</tr>
</tbody>
</table>

Results of nitrogen adsorption show that specific surface area of carbonized pyrolysis char is larger than that of calcined Ni-doped clay. The same is valid for pore volumes and average pore diameters of these materials. These data confirm that the char structure is more opened allowing for better contact with the gas phase in the reactor for model tar component decomposition.
Results of thermogravimetric analysis of Ni-doped clay and tire pyrolysis char used as catalysts for \( p \)-xylene decomposition are presented in Figure 1.

Figure 1. TG analysis of Ni-doped (3 mass\%) clay mineral calcined at 800 °C (red line) and tire pyrolysis char activated at 800 °C (violet line) catalysts in nitrogen stream.

Overall mass loss of activated clay catalyst during the TG experiment was negligible. While heating carbonized tire pyrolysis char to 800 °C with a 25 min dwell stage at this temperature, sample mass loss approached the value of 3 mass\%, majority of which occurred at temperatures exceeding 550 °C. At elevated temperatures, slow oxidation of the catalyst surface by traces of oxygen present in the gas phase could not be excluded as a change of the sample color from black to gray (ash) was observed.

Estimated bulk densities of Ni-doped clay and tire pyrolysis char catalysts were 953 kg m\(^{-3}\) and 402 kg m\(^{-3}\), respectively. Standard deviation for bulk density estimation was below 1\%. Catalyst charge with the model tar component expressed in terms of gas hourly space velocity (GHSV) was, for 10 g of tar-cracking catalysts, about 2400 h\(^{-1}\) and 1000 h\(^{-1}\) for Ni-doped clay and tire pyrolysis char, respectively.

2.2. Model Tar Component Decomposition Experiments

In experiments, the effect of reaction temperature on \( p \)-xylene decomposition was investigated in the absence as well as in the presence of the two catalysts considered. Catalyst mass applied was 10 g in individual experiments. Reaction temperatures typical for tar decomposition, i.e. 750 °C, 800 °C and 850 °C, were used. Majority of experiments were carried out in duplicate in some cases in triplicate. Relative deviations of the measured data in repeated experiments did not exceed 13\%, although their average value was below 8\%.

In Table 3, variation of \( p \)-xylene conversion with temperature and with time is recorded for both chosen catalysts. Conversion of the model tar component, \( \alpha \), was computed as a mass ratio of converted \( p \)-xylene and its input amount into the reactor:

\[
\alpha = \frac{m_{\text{xylene, in}} - m_{\text{xylene, out}}}{m_{\text{xylene, in}}} \times 100\% \tag{1}
\]

\( m_{\text{xylene, in}} \) and \( m_{\text{xylene, out}} \) denote the amount of \( p \)-xylene inserted into reactor and its output amount, respectively.
Table 3. Variation of \( p \)-xylene conversion and selectivity to toluene with reaction temperature, presence of catalysts and reaction time.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature, ( t ) [°C]</th>
<th>( p )-Xylene Conversion, ( \alpha ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau = 30 ) min</td>
<td>( \tau = 180 ) min</td>
</tr>
<tr>
<td>None</td>
<td>750</td>
<td>70.3</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>71.5</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>71.1</td>
</tr>
<tr>
<td>Ni-doped clay (10 g) ( \text{GHSV} = 2400 ) h(^{-1})</td>
<td>750</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pyrolysis char (10 g) ( \text{GHSV} = 1000 ) h(^{-1})</td>
<td>750</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Table 3 shows that simple residence time of tar-containing gaseous phase in empty reactor causes \( p \)-xylene decomposition to a relatively high level. Introduction of a catalyst can increase the tar component conversion to unity. However, catalyst activity changes with time. In the course of three hours, activity of Ni-doped clay catalyst was practically lost; meanwhile, pyrolysis char activity in \( p \)-xylene conversion at temperatures of above 800 °C was reduced imperceptibly. Still, there is some evidence of pyrolysis char activity deterioration with time. Experiments with a smaller amount of char catalyst (5 g), not presented here, were also carried out showing that \( p \)-xylene conversion decreased to 97% to 98% after 180 min of reactor operation at 800 °C. Results of the catalyst activity variation with time for experiments with 10 g of catalyst are presented in Figure 2.

![Figure 2](image_url)

**Figure 2.** Variation of \( p \)-xylene conversion with time for experiments carried out at 800 °C using 10 g of catalyst. Non-catalytic (diamonds), Ni-doped clay- (triangles) and pyrolysis char- (squares) catalyzed decomposition of model tar component.

Clay-based catalyst retained its original activity for only about 1 h of the reactor operation (Figure 2). Then, abrupt decrease of its tar-cracking ability was observed as \( p \)-xylene conversion approached the value obtained for empty reactor experiments. Similar and even faster catalyst deactivation was observed in case of toluene decomposition on Ni-doped palygorskite catalyst by Zou...
and coworkers. However, these results were obtained for slightly different reaction conditions: Ni content of 8 mass%, catalyst mass of 0.5 g and GHSV of 11323 h\(^{-1}\) [15].

Significantly higher stability was observed for the pyrolysis char-based catalyst. Catalyst activity remained unchanged within the margin of estimation error. Recently, El-Rub et al. [20] reported biomass-derived char activity in model tar component, naphthalene, decomposition. Their results show that catalyst activity was constant at 900 °C approaching full conversion of the decomposed material. However, activity of char catalyst in naphthalene decomposition passes through a minimum at 750 °C.

All condensable products from the gaseous phase were collected in IPA. Their content in the liquid samples at chosen reaction times was estimated by gas chromatography. Besides \(p\)-xylene, if present, toluene was identified as the only liquid reaction product. Its content was negligible irrespective of the reaction conditions and catalyst applied.

In Table 4, an overview of experimental results obtained at 800 °C is presented for the reaction time of 30 min. The amount of gas phase was evaluated based on the measurement of overall volumetric flow by a wet gas flow meter (model TCM 143/10, Spektrum Ltd., Czech Republic). Liquid, tar components, amount in the product stream corresponded to the increment of the liquid phase mass in scrubbers. Solid phase amount was computed to match mass balance. The amount of solid phase at the end of individual experiments was confirmed by comparing the mass of spent catalyst with coke deposits and of fresh catalyst introduced into the reactor. Samples of gas phase free of condensable components were used to estimate the content of permanent gases and lower molar mass hydrocarbons employing gas chromatography.

Table 4. Product distribution and principal components content in products of \(p\)-xylene decomposition:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>None</th>
<th>Ni-Doped Clay</th>
<th>Pyrolysis Char</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product Distribution</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid phase/%</td>
<td>1.63</td>
<td>29.13</td>
<td>27.17</td>
</tr>
<tr>
<td>Liquid phase/%</td>
<td>29.55</td>
<td>1.80</td>
<td>1.58</td>
</tr>
<tr>
<td>Gas phase/%</td>
<td>68.82</td>
<td>69.08</td>
<td>71.26</td>
</tr>
<tr>
<td><strong>Analyzed Components Content</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mass, m [g]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char</td>
<td>0.0208</td>
<td>0.3495</td>
<td>0.3450</td>
</tr>
<tr>
<td>(p)-Xylene</td>
<td>0.3481</td>
<td>0.0027</td>
<td>0.0025</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0342</td>
<td>0.0189</td>
<td>0.0175</td>
</tr>
<tr>
<td><strong>Volume fraction, (\varphi) [vol.%]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(N_2)</td>
<td>87.79</td>
<td>83.81</td>
<td>86.04</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>10.56</td>
<td>7.77</td>
<td>9.22</td>
</tr>
<tr>
<td>CO</td>
<td>0.54</td>
<td>6.06</td>
<td>2.48</td>
</tr>
<tr>
<td>(H_2)</td>
<td>0.94</td>
<td>2.23</td>
<td>1.94</td>
</tr>
<tr>
<td>(CH_4)</td>
<td>0.15</td>
<td>0.13</td>
<td>0.32</td>
</tr>
<tr>
<td>Other, (C_{2+})</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

As expected, at the given experimental conditions, the presence of catalysts caused a decrease of the amount of tar components to less than 2% of their original amount. On the other hand, the amount and composition of the gas phase was not affected to such extent. In atmosphere poor in oxidation agents, a large part of original tar components was converted to char when any of the catalysts was used. Catalyst caused only limited increase of the gaseous phase amount (1% to 3%) when confronted with the amount obtained at non-catalytic reaction conditions. For comparison, a much larger increase of the amount of gaseous products was published at conditions appropriate for steam reforming of tar in the presence of similar catalysts [15,21].

Comparing the two catalysts employed in \(p\)-xylene decomposition, higher reactivity of carbon dioxide was observed when using Ni-doped clay-based catalyst. Lower carbon dioxide and higher
carbon monoxide content in the gas phase were observed than at non-catalytic and char-catalyzed reaction conditions. It can be speculated that dry reforming of p-xylene was facilitated by the clay-based catalyst at the given conditions.

The presence of catalysts had a positive effect on the amount of hydrogen produced. Its content in the gas phase notably increased compared to that observed for non-catalytic p-xylene decomposition. The change in methane content in process gas was significant when char catalyst was used. According to Tsobouchi et al. [22] demethylation of toluene over limonite-based catalyst was notable at temperatures as low as 500 °C. At elevated temperatures, hydrocracking and reforming reactions took part in toluene decomposition. An increase of methane content in the gas phase to much lower extent was also observed in case of biomass tar catalytic decomposition by bio char [21].

In Table 4, results obtained after 30 min of the reaction are presented. Due to the large amount of char formed during the reaction, catalysts activity changed over time. Variation of gas components mole fractions with reaction time is shown in Figure 3.

The amount of hydrogen produced in the presence of heterogeneous catalysts is two- to five-times higher compared to that obtained at non-catalytic reaction conditions (Figure 3). In case of Ni-doped clay catalyst, hydrogen production passes a maximum after 90 min of the reaction, when the hydrogen volume fraction in the gas phase exceeds 4.5 vol.% (25 vol.% nitrogen-free base). Then, the content of hydrogen in process gas gradually decreased due to catalyst deactivation. Initial increase of the catalyst activity can be explained by gradual reduction of nickel oxide to the more active metallic nickel [23]. The presence of coke on the spent catalyst surface was confirmed both visually by the catalyst color change as well as by the change of its mass as given in Table 4. In a similar catalytic system used for toluene decomposition [15], an increase of hydrogen yield at the beginning of the reaction was not observed. Instead, a monotonous decrease of the hydrogen content in the process gas occurred [15]. Interestingly, apparently inactive in p-xylene decomposition (see Figure 2), clay mineral catalyst was able to promote hydrogen formation and conversion of carbon dioxide to carbon monoxide.

Activity of the pyrolysis char catalyst towards hydrogen production constantly improved in time with a maximum of approximately 3 vol.% of hydrogen (20 vol.% in the nitrogen-free gas phase). At the beginning, higher hydrogen production improvement was observed compared to its production rate at the end of the investigated time window. Further coke formation is expected to harm hydrogen production also in this case. A similar conclusion was deduced from results presented by Al-Rahbi and Williams [24]. In a two-stage gasification reactor, continuous increase of hydrogen production was observed with the system operation time. Into the gas phase produced from biomass in the first reactor stage, extra amount of steam was added. At these conditions, however, volume fraction of hydrogen was larger (about 40 vol.% on the N₂-free base) [24]. According to data shown in Figure 3, the content of methane in process gas obtained in the presence of Ni-doped clay catalyst was lower compared to that observed at non-catalytic reaction conditions. This may prove that the presence of clay-based catalyst does not favor p-xylene demethylation as shown by the results of Zou and coworkers [15]. On the other hand, a higher amount of methane was found when using pyrolysis char catalyst for p-xylene abatement. This observation is in line with that of Al-Rahbi and Williams, although no defined tars were decomposed in their experimental study over a tire pyrolysis char catalyst [24].

Both catalysts employed in this study were able to activate reactions of CO₂ with p-xylene or its decomposition products; Ni-based clay catalyst was more efficient (Figure 3). Thus, the amount of carbon dioxide in the process gas produced was lower compared to the nominal one. It seems also that the employed catalysts activated dry reforming and/or Boudouard reactions as the decrease of carbon dioxide content in process gas was outbalanced by the increase of carbon monoxide content.

It also can be concluded that the presence of catalysts suppressed the formation of lower hydrocarbons. In case of the clay-based catalyst, the content of C₂⁺ hydrocarbons in the process gas was negligible. In the gas stream from reactor containing pyrolysis char, the content of these hydrocarbons was apparent after about 90 min of the reactor operation.
Figure 3. Variation of hydrogen (a), methane (b), carbon dioxide (c), carbon monoxide (d) and C$_{2+}$ hydrocarbons (e) content in process gas with reaction time for non-catalytic (diamonds), Ni-doped clay- (triangles) and pyrolysis char- (squares) catalyzed p-xylene decomposition. Results obtained using (0 g) 10 g of catalysts at 800 ºC.
3. Materials and Methods

Technical gases, nitrogen and carbon dioxide, were supplied by Messer Tatragas, Bratislava, Slovakia; their purity was above 99.9 vol.% and 99.5 vol.%, respectively. p-Xylene (p.a., GC purity above 99.5%) was purchased from Reachim, Moscow, Russia. Tap water was used for the humidification of model process gas entering the reactor for tar component decomposition. Clay mineral used as the catalyst and support for nickel-based tar-cracking catalyst originated in the Mahammad Agha region in the Logar province of Afghanistan. Char obtained from mixed automobile and truck tires by their pyrolysis at 550 °C and used as a catalyst for model tar component decomposition was supplied by DRON Industries, Dunajská Streda, Slovakia. Ni(NO$_3$)$_2$·6H$_2$O (purum) was purchased from Lachema, Brno, Czech Republic. Propan-2-ol (purity above 99.7 mass%) used for tar components capture from the product gas was supplied by Centralchem, Banská Bystrica, Slovakia.

3.1. Catalysts Preparation and Characterization

Clay-based catalyst (Figure 4a) was prepared by the incipient wetness impregnation procedure using a solution of Ni(NO$_3$)$_2$ to provide a catalyst containing 3 mass% of Ni. Natural clay particles between 0.8 mm and 2 mm obtained by crushing larger pieces of rock mineral and sieving were used for this purpose. As prepared catalyst was dried at 105 °C for 2 h in air and calcined at 800 °C for 6 h in flowing nitrogen according to the procedure described by Šuhaj and coworkers [16]. Active metal content in the catalyst was confirmed by the TG analysis. During the calcination of Ni-impregnated clay mineral, about 15 mass% of the sample were lost due to the raw catalyst surface changes and decomposition of nickel nitrate supported on its surface [16].

![Particulate clay (a) and tire pyrolysis char (b) used for the catalyst preparation for model tar component decomposition.](image)

Pyrolytic char catalyst (Figure 4b) was prepared from char powder. Raw material was compacted using a roll compactor for powder materials providing a solid plate of compacted material, which was then shredded, and particles with a diameter in the range from 3–5 mm were separated by sieving. Compacted particles were then dried in an oven at 105 °C for 6 h. Dried particles were activated at the temperature of 800 °C for 4 h in CO$_2$ atmosphere.

Raw pyrolysis char contained a large amount of organic material which blocked the char porous structure and also certain amount of inorganic compounds. In order to evaluate the content of both organic and inorganic material, TG analysis of raw pyrolysis char was carried out. First part of the analysis was realized in an inert atmosphere to determine the amount of volatiles. Then, a sample of char was fired in oxidation atmosphere to check the content of ash.
Char porous structure was freed of the majority of volatiles (about 26.3 mass%) during the catalyst activation step. Additionally, catalyst mass decreased by about 3 mass% due to oxidation of its surface by carbon dioxide. This value was confirmed by a separate TG experiment [17]. Then, the sample overall mass loss during carbonization (volatiles release + char surface oxidation with carbon dioxide) reached approximately 29.3 mass%. This finding is consistent with the observations of Mui and coworkers [25] who stated that prolonged carbon dioxide treatment of chars causes deterioration of its internal structure due to excessive oxidation of pore walls. Thus, optimum char activation time should be found in order to assure the best char-derived catalyst performance in tar decomposition reactions. Details of pyrolysis char-based catalyst preparation and characterization are given in literature [17].

Composition of clay- and pyrolysis char-based catalysts was estimated by X-ray fluorescence analysis using a SPECTRO X-LAB 2000 spectrometer (SPECTRO Analytical Instruments Inc., Kleve, Germany), X-ray diffraction analysis using a Theta/Theta X-ray diffractometer (STOE, Darmstadt, Germany) and elemental analysis employing a CHNOS analyzer vario MACRO cube (Elementar, Langenselbold, Germany). Metal content in pyrolysis char was determined using an atomic emission spectrometer with microwave plasma Agilent MP-AES 4100 (Agilent Technologies, Santa Clara, CA, USA). Microstructure properties of the prepared catalysts were characterized using a Surfer gas adsorption porosimeter (Thermo Scientific, Waltham, MA, USA). Thermogravimetric analysis of the catalysts was performed using a STA 409 PC Luxx thermogravimetric apparatus (NETZSCH, Selb, Germany). Detailed procedures of these analyses were given elsewhere [16,17]. Bulk density of both catalysts was estimated by precisely weighing a known volume of packed solid samples.

3.2. Experimental Set-Up of Model Tar Component Decomposition Unit

*p*-Xylene decomposition experiments were carried out at the conditions of simulated processing gas environment in the set-up shown in Figure 5.

![Figure 5. Flow-sheet of unit used for model tar component catalytic decomposition: pressure cylinders with N$_2$ (1) and CO$_2$ (2), mass flow-meters (3, 4), thermostated (28 °C) scrubbers for gas phase saturation with water vapor (5), scrubber for water droplets separation (6), *p*-xylene reservoir (7), peristaltic pump (8), heated (150 °C) flask for *p*-xylene evaporation (9), electrically heated reactor (10) with catalytic (10a) and supporting (10b) layers, scrubber with IPA at ambient temperature (11), thermostated (37 °C) scrubbers with IPA for capture of condensable components from gas phase (12), cryostated (−20 °C) scrubbers with IPA and glass balls (13), gas phase sampling port (14), wet gas flow meter and exhaust (15).
The effect of reaction conditions, temperature, the presence of catalyst and time on the model tar component decomposition, products’ distribution and composition was investigated. Temperature range of 750–850 °C was applied in these experiments. The amount of catalyst employed in model tar component cracking experiments was 10 g. Experiments were prolonged for up to 3 h.

Gaseous feed stream (approximately 25 L h⁻¹, room temperature) entering the reactor for model tar component decomposition contained N₂ (85 vol.%), CO₂ (10 vol.%), H₂O (3 vol.%) and p-xylene (2 vol.%). Composition of this stream was adjusted using mass flowmeters for permanent gases, pre-set temperature in thermostat for gas phase saturation with water vapors and a peristaltic pump used for p-xylene admixture (see Figure 5). Gaseous phase leaving the reactor passed through a series of scrubbers containing propan-2-ol (isopropanol, IPA) at different temperatures. Here, condensable components of the product stream were captured for subsequent analysis in a gas chromatograph. Samples of the gas phase free of tar components were taken by a syringe right behind the last scrubber. Gas phase composition was estimated chromatographically using an Agilent 7890A gas chromatograph (Agilent Technologies, Santa Clara, CA, USA). Liquid samples obtained by pouring together the content of all scrubbers with IPA were analyzed on an Agilent 6890N gas chromatograph (Agilent Technologies, Santa Clara, CA, USA). Conditions at which these analyses were carried out are described in detail in literature [17].

4. Conclusions

Initial activity of both tested catalysts (Ni-based clay and pyrolysis char) was similar. Complete decomposition of the model tar component, p-xylene, was achieved using 10 g of the catalyst at the reaction temperature of 800 °C. Activity of the pyrolysis char catalyst was stable for at least 3 h while Ni-based clay catalyst deactivation was observed after 1 h of the reactor operation. In comparison with non-catalytic reaction conditions, almost complete conversion of p-xylene was achieved. These results are consistent with previously published data for similar catalytic systems [15,20].

From the presented product distribution analyses, it can be concluded that the extra amount of model tar component converted in the presence of catalysts is primarily converted to coke. At the given experimental conditions, only a small part of the model tar component was converted to gaseous products. Ni-based clay catalyst caused an increase of carbon dioxide reactivity in dry reforming and/or Boudouard reactions, thus enabling its conversion to carbon monoxide. At the same time, relatively significant increase of the amount of produced hydrogen was observed. While using the clay-based catalyst, hydrogen evolution rate passed a maximum of over 4.5 vol.% in process gas stream (about 25 vol.%, N₂-free gas phase) after 90 min. Demethylation of the model tar compound in the presence of the selected catalysts was not favored.

Hydrogen content in process gas gradually improved without signs of perceptible deactivation using the char-based catalyst. After 3 h of the reactor operation it reached 3 vol.% (15 vol.% on N₂-free base). On the other hand, activation of carbon dioxide by the pyrolysis char catalyst was marginal compared to that observed for the clay-based catalyst. In the presence of the char catalyst, lower but appreciable amount of methane was formed at the given reaction conditions. After 90 min of the reactor operation, stable methane and C₂+ hydrocarbons content of 0.6 vol.% and 0.02 vol.% respectively, was observed in process gas. Moreover, in this case, deposits of coke formed on the catalyst surface caused alteration of its activity.

While reaching full conversion of the model tar component, liquid phase from the gaseous stream contained mostly toluene and only traces of unreacted p-xylene. Deactivation of clay catalyst towards p-xylene decomposition was caused by coke formation. However, even then hydrogen evolution in the reactor was not stopped and carbon dioxide conversion to carbon monoxide continued. In the presence of char-based catalyst, production of toluene was low, and it was further diminished along with the reaction time and with the increasing reaction temperature.

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