

# Catalytic Gasification of Different Pre-treated Waste Rubbers to Obtain Syngas

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Waste tires represent a significant environmental burden, the further value-added use of which has not been solved. Among the energetic utilization, combustion and pyrolysis are used. During combustion, a significant amount of SO<sub>x</sub> can be released into the environment. During the pyrolysis of waste rubber, the amount of liquid product is significant, which consists of mainly aromatic and cyclic hydrocarbons. Furthermore, the sulphur content of liquid products is also significant. On the other hand, high-temperature gasification of rubber waste can be a promising solution for the production of hydrogen, synthesis gas and other hydrocarbons. During gasification, gaseous products and solid residues are produced, and the amount of liquid products is very small. The amount of hydrogen and synthesis gas can also be increased by catalysts and steam. This work focuses on the high temperature gasification of waste tires obtained by different pre-treating methods. Waste rubber samples were recycled in a laboratory scale gasifier using steam and transition metal loaded catalyst. Gases contain hydrogen and CO. The presence of steam and transition metal containing catalyst had significant effect to the product yield, however the samples pre-treating had less effect to the decomposition reactions. The thermal decomposition of raw materials was also followed by mathematical calculations.

Keywords: waste tire, gasification, hydrogen

## 1. Introduction

Due to increasing living standards in modern societies, a significant amount of rubber waste is generated in each year. In 2024, nearly 23 million tons of tyre were produced, which significantly can pollute the environment at the end of their life cycle [Czarna-Juszkiewicz et al. 2023, Smithers 2024]. Tires represent a significant part of rubber waste, of which less than a third is recycled [Czarna-Juszkiewicz et al. 2023, Hu et al. 2024]. Among the recycling methods, energetic, mechanical and chemical methods are the most significant [Xiao et al. 2022, Pei et al. 2024]. Nowadays, still the energy utilization mostly means waste incineration [Pei et al. 2024]. However, due to the sulphur and other elemental content of rubber waste, their burning significantly increases the amount of sulphur-containing substances entering the environment. Regarding the mechanical recycling of waste rubber, the biggest challenge is to guarantee the constant product quality and a stable market [Arabiourrutia et al. 2020]. On the other hand, depending on the reaction parameters to be used, various valuable products can be obtained by the chemical utilization of rubber waste. The chemical recycling is a thermal process, in which the long carbon chain of the raw materials should be transformed into substances with lower molecular weight (e.g. hydrocarbon gases, pyrolysis oil) and carbon black [Oboirie et al. 2017]. At lower temperature, pyrolysis oil has high yield, while gas product is the most significant at high temperature. Above 800°C, in the presence of steam and a catalyst, synthesis gas with a high hydrogen content can also be obtained from rubber waste [Li et al. 2024]. It is also known, that transition metals on catalyst supporter with high specific area mostly applied as catalysts for gasification [Fajimi et al. 2024]. Relatively lots of information is available about the effect of catalysts and operational parameters on product characteristics, but only a limited

number of studies have investigated the effect of raw material preparation [Oboirie et al. 2017, Arabiourrutia et al. 2020]. In this work, the pre-treatment of rubber waste and its effect to the gasification and product characteristic was investigated in laboratory scale reactor.

## 2. Materials & methods

### 2.1 Raw material

In this work, five different waste rubber samples were used. In case of chemical treating, the mechanically pre-treated rubber was put into a Re-1 prototype reactor (Re-Tyre GmbH, Linz, Austria). After filling up the reactor, the reactor chamber was closed and filled up with ozone gas using OG-9 Type ozone generator (Re-Tyre GmbH, Linz, Austria). Ozonolysis was carried out for 8 hours with regular mechanical mixing. At the end of the treatment, the ozone was destroyed by the EI-3 device. The resulting rubber shred fractions were separated by size exclusion filters. The mechanical shredding of tires were carried out by using standard commercial mechanical shredders. Samples were treated as following:

- S-1: Fork lift tire treated by ozonolysis sample size up to 3mm
- S-2: Passenger car tire rubber treated with mechanical shredding
- S-3: Passenger car tire rubber treated by ozonolysis sample size up to 3mm
- S-4: Fork lift tire treated by ozonolysis sample size 3-5 mm
- S-5: Mixed vehicle tire treated by ozonolysis, sample size up to 3 mm

Based on CHNS analysis, the carbon content of S-1, S-2, S-3, S-4 and S-5 samples was 81.3, 82.4, 86.6, 87.0 and 84.2%, while that of sulphur 0.8, 1.7, 1.5, 1.0 and 1.0%, respectively. Samples contain also 0.3-1.1% nitrogen and 6.9-8.0% hydrogen.

To promote the thermal decomposition of raw materials, Ni/ZSM-5 catalyst was applied. The Ni/ZSM-5 catalyst was prepared by wet impregnation using 1M Ni(NO<sub>2</sub>)<sub>2</sub>·6H<sub>2</sub>O solution at 80°C for 3 hours. After that, the suspension was filtered and dried at 110°C for 10 hours. Finally, the treated catalysts were calcined at 600°C for 3 hours. The catalyst has 330m<sup>2</sup>/g BET surface and 210m<sup>2</sup>/g microporous surface areas, the Si/Al ratio was 19.

### 2.2 Reaction kinetic calculation

The main reaction kinetic parameters of the waste rubber pyrolysis were calculated based in thermogravimetric analysis. The raw materials were investigated using TG 209 F1 Libra equipment. The temperature range was 30-900°C, the heating rate was 50°C/min and the nitrogen flow was 20 mL/min. The activation energy of the thermal decomposition was calculated by the following equation:

$$\frac{dx}{dt} = A \cdot e^{\left(\frac{-E}{RT}\right)}(1 - x)$$

where "A" is the pre-exponential factor, "E" is the activation energy, "T" is the temperature, "t" is the time for reaction "x" is the conversion, and "R" is the universal gas constant.

Based on the results obtained from the thermogravimetric analysis of raw materials, Table 1 shows the main temperatures, the pre-exponential coefficient and the calculated activation energies of thermal decomposition. T<sub>i</sub> and T<sub>f</sub> is the initial and final temperature of weight change, respectively. T<sub>max</sub> is the temperature, where the DTG curve has maximum. Significant differences were found among the activation energies of the thermal decomposition of the individual samples. All samples were decomposed in two steps. The temperature range of the first step was 305-453°C without catalyst, and that of the second step was 433-530°C. Without catalyst, S-2 sample has the highest activation energy. In the presence of Ni/ZSM-5 catalyst, the activation energies decreased in all cases, and the decomposition temperature range shifted towards the lower values. This result was contributed to the effect of catalyst on reducing the energy required for initial reaction. In case of the first step of decomposition, the temperature range was between 264-415°C, and in the second between 426-543°C with catalyst. In the first reaction step the primary reactions were taken place resulting aliphatic and aromatic compounds, while the further decomposition of the compounds obtained from the first reaction step decomposed further in the temperature above 400°C. Results well demonstrate, that the Ni/SM-5 catalyst primarily reduced the initial temperature of the first decomposition step. On the other hand, in the presence of catalyst, there was a significant decrease in activation energies for both decomposition steps. Regarding the second reaction step, the most significant decreasing in activation energy was found in case of S-2 and S-3 samples.

Table 1: The main results of TG analyses of rubber samples

		Without catalyst					With catalyst				
		S-1	S-2	S-3	S-4	S-5	S-1	S-2	S-3	S-4	S-5
1 <sup>st</sup> step	T <sub>i</sub> , °C	311	327	312	275	318	275	302	271	300	283
	T <sub>max.</sub> , °C	402	411	403	405	408	390	400	415	405	406
	T <sub>f</sub> , °C	434	438	436	442	442	435	437	422	435	433
	A	0,61	0,78	4,52	5,80	4,63	2,59	1,15	2,36	4,51	2,50
	E <sub>a</sub> , kJ/mol	68	63	54	48	57	59	63	57	40	57
2 <sup>nd</sup> step	T <sub>i</sub> , °C	435	433	438	445	442	435	441	426	437	432
	T <sub>max.</sub> , °C	460	475	468	460	467	457	453	461	460	452
	T <sub>f</sub> , °C	510	528	515	520	530	521	536	533	520	543
	A	5,72	4,05	0,19	7,15	6,22	9,83	11,30	10,25	4,83	12,59
	E <sub>a</sub> , kJ/mol	41	56	66	38	40	35	37	38	32	36

### 2.3 Gasification

The waste rubber samples have been gasified at 800°C under nitrogen, then the volatiles were passed through a Ni-ZSM-5 catalyst bed, which temperature was 700°C.

In case of catalytic experiment, water was also added into the reactor with 5g/h flow rate. The raw material catalyst ratio was 2:1. Volatiles from the tubular reactor was passed through a water bath, then gases was collected in Tedlar bag for further analysis. The composition of gases was analysed by DANI type gas chromatographs (GC-FID (Rtx-1 PONA type 100 m long column with an internal diameter of 0.25 mm and film thickness of 0.5 µm) and GC-TCD (Carboxen™ 1006 PLOT (30m×0.53mm) column)). The chromatograms were evaluated using Clarity software.

## 3. Results & discussion

### 3.1 Product yield

The yields of products are summarized in Figures 1 and 2. Based on the results, it is clear that in the presence of water vapor, more gas products and liquid products were formed in all cases.

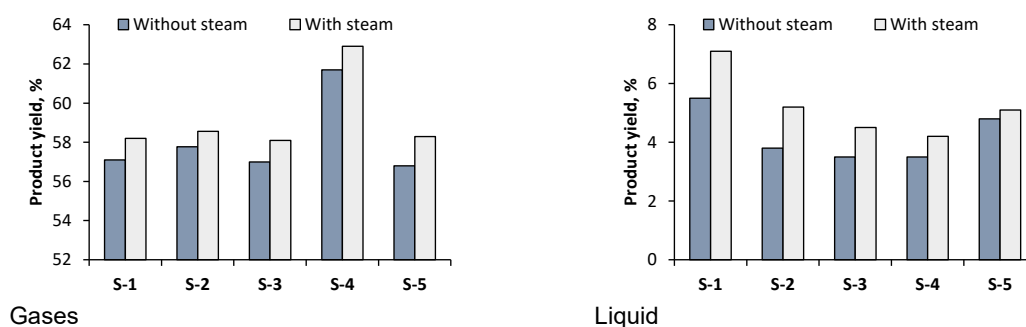


Figure 1: The yields of products without catalyst

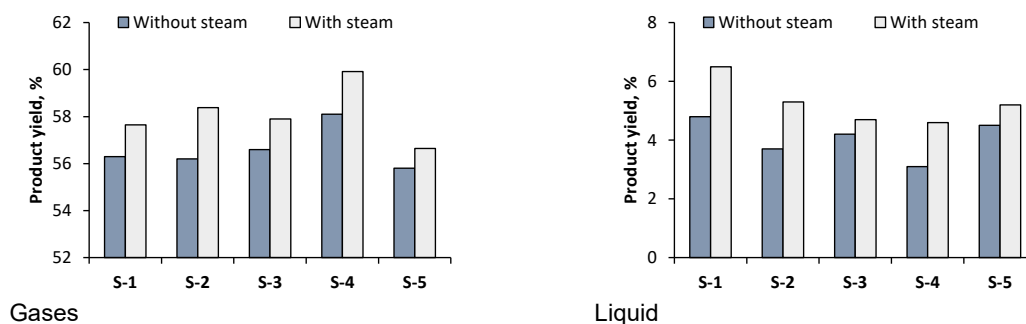


Figure 2: The yields of products with Ni/ZSM-5 catalyst

Most gas products were obtained from the S-4 sample both without and in the presence of the Ni/ZSM-5 catalyst. In terms of liquid products, sample S-1 has the highest, while sample S-4 has the least yield. It is worth to mentioned, that the liquid phase was the mixture of hydrocarbon and aqueous phase.

### 3.2 Gases

The composition of gases are demonstrated in Figures 3 and 4. Without water vapor, the gas products contained hydrogen, methane and C<sub>2</sub>-C<sub>5</sub> hydrocarbons. CO and CO<sub>2</sub> were only present in the gas products when the raw materials were gasified using steam. The reason for this phenomena was, that the structure of rubber has no oxygen. In all cases, less hydrogen was obtained without a catalyst than in its presence. Without catalyst, the hydrogen content varied between 26.2-28.7% (without steam) and 29.8-33.2% (with steam). The hydrogen content was between 21.6-27.3% (without steam) and 34.9-38.4% (with steam), if Ni/ZSM-5 catalyst was also present during the gasification. In case of thermo-catalytic gasification, the amount of C<sub>2</sub>-C<sub>5</sub> hydrocarbons was significantly lower, because hydrocarbons transformed into hydrogen and CO. On the other hand, the pre-treatment of rubber waste had no significant effect on the composition of the gas products. In the presence of catalyst, not only the amount of hydrogen but also CO was higher than without. The CO<sub>2</sub> content of the gases could be also reduced by the Ni/ZSM-5 catalyst. Presumably it was the consequence of the dry reforming reactions resulted higher concentration of hydrogen and CO. Both the application of steam and the Ni/ZSM-5 catalyst can increase the yield of methane.

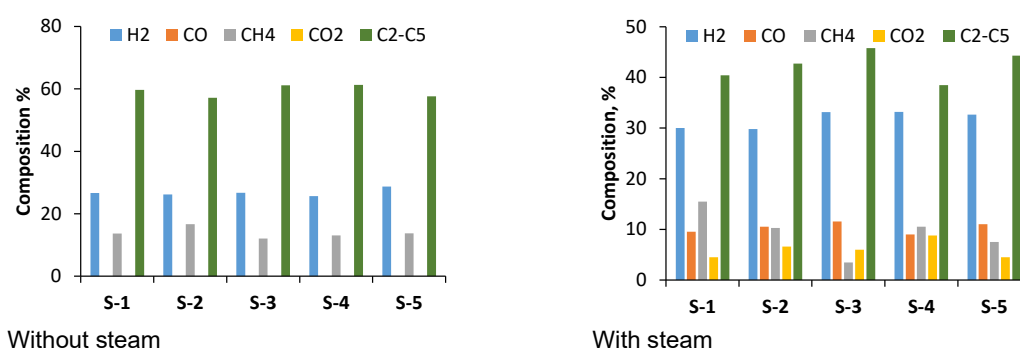


Figure 3: The composition of gases without catalyst

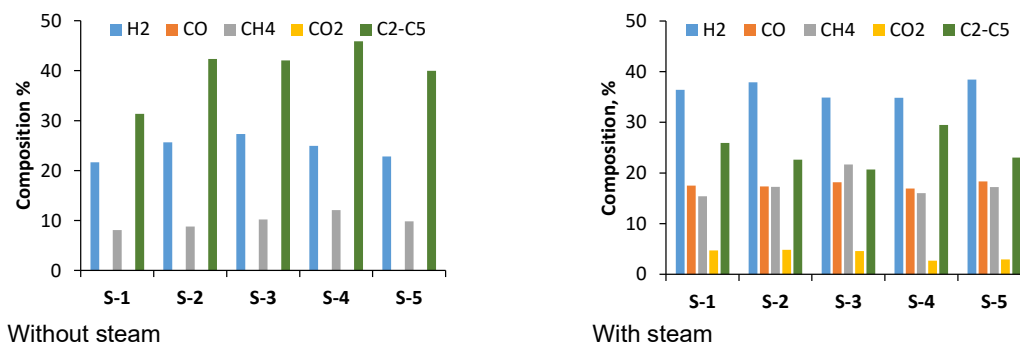


Figure 4: The composition of gases with Ni/ZSM-5 catalyst

Figures 5 and 6 show the syngas yield. As it was demonstrated earlier, gases has no CO and CO<sub>2</sub> without steam, therefore the syngas has only hydrogen content in these cases. That is the cause for the significantly lower syngas yield obtained without steam, however the presence of steam during the gasification can also increase the yield of hydrogen. The syngas yield was significantly less, than that of in the presence of catalyst both in absence and presence of steam. E.g. it was 30.4-32.6 mmol/g raw material without catalyst and steam, which increased to 62.2-64.5 mmol/g raw material in the presence of Ni/ZSM-5 catalyst and steam. However, there was no significant difference among the syngas yield from different pre-treatment of rubber samples. The ratio of hydrogen and CO was in the range of 1.92 and 2.28 in the presence of Ni/ZSM-5 catalyst, which refer to the similar chemical reactions resulting hydrogen and CO. However, the ratio was between 2.83 and 3.68 without catalyst. The ratio of syngas components is a key property for further application of gases obtained from

waste gasification, because the ratio of hydrogen and CO as raw materials in case of different products obtained from syngas has significant difference.

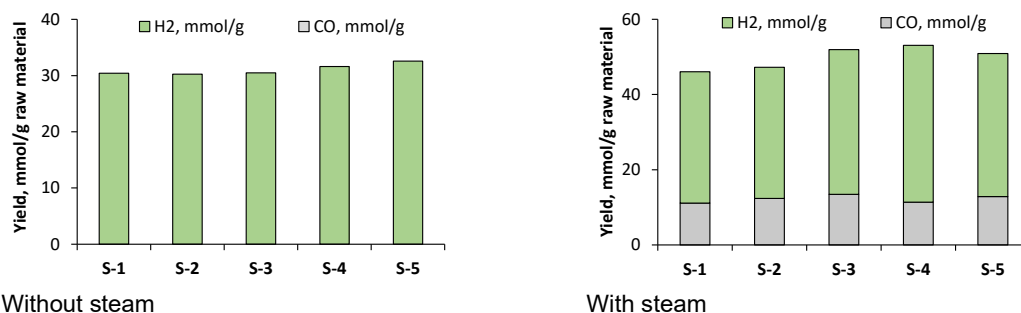


Figure 5: The yield of syngas without catalyst

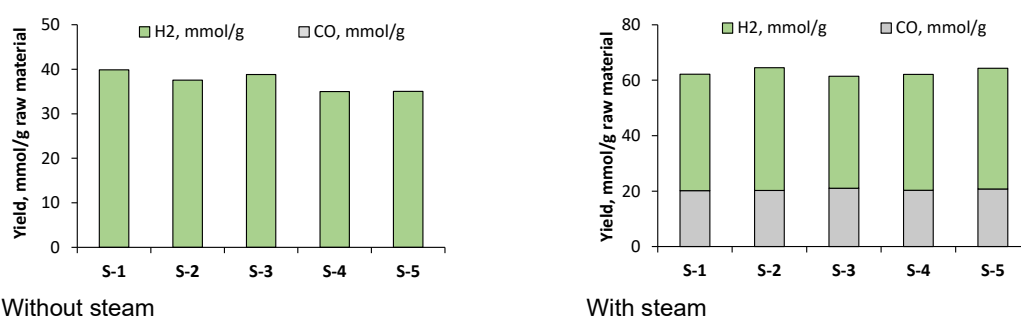


Figure 6: The yield of syngas with Ni/ZSM-5 catalyst

### 3.3 Char

The morphology of the chars remaining in the reactor after the pyrolysis are shown in Figure 7. The surface of black color char was rather bordered by sharp, flat plates and the grain size has wide distribution.

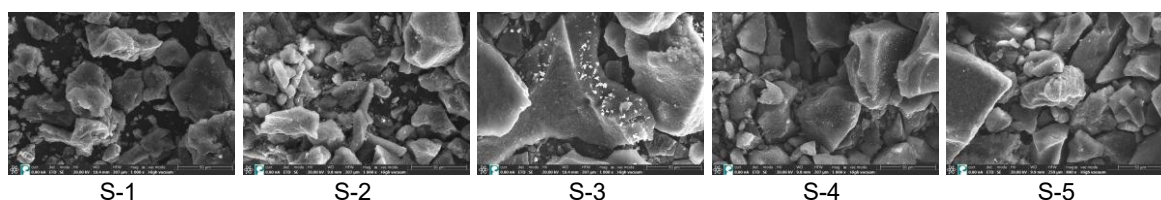


Figure 7: The morphology of char at the end of gasification

The elemental composition of char samples is summarized in Table 2. Compared to the raw materials, the carbon content of the char decreased slightly in all cases, and the hydrogen content was significantly lower. The sulphur content of the char samples increased by at least three times compared to the raw samples, which was the consequence of the enrichment of sulphur-containing components in the solid product. Regarding the nitrogen content, a decrease could be observed compared to the raw materials.

Table 2: The composition of char samples

	S-1	S-2	S-3	S-4	S-5
<b>C</b>	78.9	81.9	84.2	84.9	82.2
<b>H</b>	1.8	1.1	1.1	0.9	0.1
<b>N</b>	0.6	0.2	0.1	0.2	0.2
<b>S</b>	3.6	3.1	2.5	3.1	3.1

### 3.4 Catalysts

The surface of the catalysts after the gasification are shown Figure 8. The catalyst had a spherical geometry, which did not change during the gasification. The pictures clearly show that the catalyst was agglomerated in many places, and that smaller deposits were also observed on the surface of several catalyst grains. It was presumably coke deposition formed in the gasification reactions.

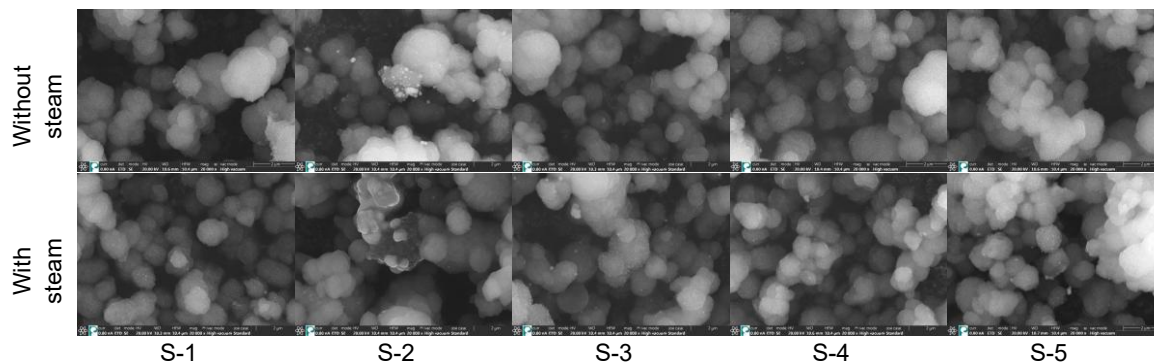


Figure 8: The morphology of catalysts at the end of gasification

### 4. Conclusions

In this work, the gasification of different pre-treated waste tires had been investigated in a laboratory scale reactor using Ni/ZSM-5 catalyst. It was found, that gases contained significant amount of hydrogen and CO. However CO was obtained only in the presence of steam. Regarding the pre-treating of raw material no significant differences were found among the properties of different products. Gasification results liquids beside gases. Raw materials were decomposed in two steps, the temperature range of the first step was 305-453°C, and that of the second step was 433-530°C. The activation energy of the first step was 48-68kJ/mol, while that of 40-63kJ/mol in the second step without catalyst. Each activation energy can be decreased by catalysts and the lowest was calculated using the S-4 samples.

### Acknowledgments

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