DOCTORAL (PhD) DISSERTATION THESES

VALUE-ADDED TRANSFORMATION OF BIOMASS-BASED WASTE INTO SYNTHESIS GAS

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1. INTRODUCTION AND OBJECTIVES

The fight against climate change and the urgent need to reduce the environmental burden significantly encouraged the exploration of sustainable and environmentally friendly alternative energy sources. Among these alternatives, biomass is a promising solution due to its renewable nature and ability to significantly reduce greenhouse gas emissions.

Even though biomass is a renewable energy source, its cultivation, collection and processing can have harmful environmental effects. In addition, during the burning of biomass, pollutants and substances which are harmful to the environment, e.g. solid particles, nitrogen oxides and volatile organic compounds may be released. Biomass gasification is a promising technology to solve these problems, but the used catalysts and adsorbents in the process play a critical role in increasing the process efficiency and reducing the emission of harmful substances.

During the gasification of biomass, various sorbents are utilized to capture the produced carbon dioxide. Adsorbents capture carbon dioxide molecules through physical or chemical interactions, preventing their emission into the atmosphere.

In the doctoral dissertation, the thermal and thermo-catalytic gasification of agricultural biomass, with steam and without steam was investigated, in order to increase the synthesis gas yield and reduce carbon dioxide emissions. During the research work, to enhance the process efficiency, the possibility of reusing the used catalysts was also studied. In addition, to further decrement of carbon dioxide content, different adsorbents were used, whose reusability and impact assessment were monitored through regeneration cycles.

2. EXPERIMENTAL WORK

The purpose the experimental work was to investigate the composition of the obtained synthesis gas during the gasification of different biomass and to reduce the amount of carbon dioxide. The thermal degradation of five different raw materials was investigated between 200-800°C where the carbon dioxide capturing effect was studied in case of four different adsorbents, using a model gas mixture. Regarding the investigation of raw materials, the main aim was to select a widely available material, that has an adequate lignocellulose content, also, a significant amount of hydrogen and carbon monoxide is produced during its gasification. Therefore, the effect of the moisture content of raw material on the product composition and energy consumption was examined, while during the investigation of adsorption of CO_2 the most effective adsorbent was selected and its cyclic carbon dioxide capturing capacity was studied.

The effect of the main gasification parameters (steam:biomass ratio, temperature, catalysts) on the product composition and the synthesis gas yield was also investigated. At first, the temperature of the 1st and then the 2nd reactor zone was determined, after the effect of the steam:biomass ratio in the range of 0.2-1.8 was investigated. As catalyst, a natural zeolite, a synthetic zeolite, a mesoporous material and a carbon dioxide capturing material was chosen, on which nickel by wet impregnation was applied, and the effect of the individual catalysts and its regeneration cycles was examined (Ni/Clinoptilolite (4,9 Si/Al ratio, 18 m^2/g specific surface area); Ni/ZSM-5 (18,6 Si/Al ratio, 335 m^2/g specific surface area); Ni/Al_2O_3 (0,6 m^2/g specific surface area); Ni/CaO (55 m^2/g specific surface area)).

During the experiments, a low and a high-temperature measuring point was determined, where the synthesis gas yield was significant with steam. Finally, the two best catalysts were chosen and the most effective adsorbent was placed in a post-situ way into the gasification process, for further carbon dioxide content decrement.

3. NEW SCIENTIFIC RESULTS

3.1. The investigation of moisture content of raw material

It was found that during the gasification by the mixing of the examined maize biomass and the used Ni/ZSM-5 catalyst, in the presence of steam at a lower temperature (200-500°C), with 0% and 20% moisture content, carbon dioxide and C_2-C_5 hydrocarbons were the dominant components. Furthermore, the highest hydrogen yield was produced at 40% moisture content, and that of the H_2/CO ratio could be maximized at 900°C. Under the same conditions, the highest amount of synthesis gas was produced from the raw material without moisture content, and in this case the CO/CO_2 ratio was the highest.

3.2. Adsorption experiments

a) It was found that the tested, not the ones as references, adsorbents (NaX with 0.03 Si/Al ratio, 15.9 m^2/g specific surface area, Zeosorb 5A with 1.5 Si/Al ratio, 448.2 m^2/g specific surface area, 3.9 Si /Al ratio, Clinoptilolite with a specific surface of 16.5 m^2/g), Clinoptilolite had the highest CO_2 capacity; 1.5 mmol CO_2/g at 0°C, 1.1 mmol CO_2/g at 30°C, and 0.8 mmol CO_2/g at 60°C. The CO_2 capturing capacity was changed significantly in case of the studied Clinoptilolite (Ca-type, formula: $KNa_2Ca_2(Si_9Al_7)O_{72}•24H_2O$) as a result of temperature changes. The investigated Clinoptilolite initially contained 44% clinoptilolite, 8% crystal balite, 24% sanidine, and 23% amorphous phase, in which the crystal water content in the Clinoptilolite structure decreased significantly with increasing temperature above 200°C. Besides, above 500°C in the natural zeolite the proportion of clinoptilolite was decreased significantly, while that of the amorphous and sanidine phases increased. In the case of low heat treatment (<200°C), the water content in the Clinoptilolite structure was disadvantageous in terms of CO_2 capturing capacity.

b) It was observed that with the increment of treatment temperature of Clinoptilolite, its carbon dioxide capacity showed continuous improvement as the regeneration cycles progressed up to 400°C (~60% increase in capacity), then in case of 600°C and 800°C a decrease in capacity was detected as a result of a structural change. In addition to the changes in the structure, the CO_2 capturing capacity of the tested Clinoptilolite showed an enhanced tendency due to the increment of its specific surface are (especially the microporous surface area) due to the miniaturization caused by the multiple regeneration.

3.3. Gasification preexperiments

a) It was found, that during the thermal degradation (between 200-800°C) of the examined maize biomass, the yield of hydrogen and methane increased by nearly 25% as the enhancement of temperature. Utilizing 400°C in the 1st reactor zone, the hydrogen yield was the highest in the presence of Ni/CaO and Ni/Cinoptilolite catalysts, while the greatest carbon monoxide and synthesis gas content occurred in the presence of Ni/Clinoptilolite.

b) It was showed that during the gasification of the used agricultural biomass, until steam:biomass ratio = 1 with Ni/ZSM-5, the amount of carbon monoxide and carbon dioxide decreased by the increment of steam:biomass ratio, while the presence of Ni/CaO carbon monoxide and hydrogen yield was increased, while in the presence of Ni/Clinoptilolite the H_2/CO ratio was the highest.

3.4. Gasification experiments

With my experimental results, it was proved that the activity of the tested catalysts (Ni/ZSM-5, Ni/Al_2O_3, Ni/CaO and Ni/Clinoptilolite) in gasification reactions differed significantly from each other, on the other hand, the effect on gas composition and yield was also significantly influenced by the temperature of the reactor zones and the regeneration cycles.

a) It was determined that at temperatures of 400°C in the first reactor zone and 700°C in the second reactor zone (without steam), the amount of carbon dioxide was significantly reduced through 10 regeneration cycles in the examined Ni/ZSM-5. The amount of carbon monoxide was observed to decrease with the regeneration cycles. Regarding the hydrogen content, it was found that in the presence of Ni/ZSM-5, an increasing trend was observed during the 4th to 9th regeneration cycles. During low-temperature catalytic gasification (in the presence of steam), the amount of carbon monoxide could be reduced starting from the 4th-5th regeneration cycles, while the carbon dioxide content decreased in each cycle beginning with the 2nd cycle. Concerning the hydrogen content, it was established that an increase could be achieved during the first regeneration cycle in the presence of Ni/ZSM-5. During high-temperature catalytic gasification (without steam), the amount of carbon dioxide could be significantly reduced as the regeneration cycles progressed, while the amount of carbon monoxide could be increased in each of the regeneration cycles. During high-temperature catalytic gasification (in the presence of steam), the carbon dioxide content increased as the regeneration cycles progressed, while the carbon monoxide content exhibited a significant decrease depending on the regeneration cycles. The generally decreasing carbon dioxide and hydrogen content, along with the increasing CO content, can be explained by the catalyst's high

Si/Al ratio, specific surface area, and acidity, while the increasing hydrogen content is attributed to the nickel content and high Si/Al ratio of the catalyst.

b) It was determined that at temperatures of 400°C in the first reactor zone and 700°C in the second reactor zone (without steam), the amount of carbon dioxide was significantly reduced through 10 regeneration cycles in the examined Ni/Al_2O_3. The amount of carbon monoxide was observed to change with a decreasing trend during the regeneration cycles. Regarding the hydrogen content, an increasing trend was observed during the 4^{th} to 9^{th} regeneration cycles. During low-temperature catalytic gasification (with steam), the amount of carbon dioxide could be reduced starting from the 4^{th} and 5^{th} regeneration cycles. The hydrogen content showed increasing values in each of the regeneration cycles. During high-temperature catalytic gasification (without steam), the carbon monoxide content decreased in each regeneration cycle, while the CO_2 content increased. The hydrogen content exhibited increasing values during the 2^{nd} to 7^{th} regeneration cycles. During high-temperature catalytic steam gasification, the carbon dioxide content could be reduced between the 1^{st} and 2^{nd} cycles as the regeneration cycles progressed, while the carbon monoxide and hydrogen content showed a significant decrease depending on the regeneration cycles. The slight effects of the catalyst can be explained by its small specific surface area, and the slight decrease in carbon dioxide content is attributed to catalyst sintering, leading to the formation of micropores.

c) It was determined that at temperatures of 400°C in the first reactor zone and 700°C in the second reactor zone without steam, the amount of carbon dioxide was significantly reduced through 10 regeneration cycles with Ni/Clinoptilolite. The amount of carbon monoxide increased until the 6^{th} regeneration cycle and then decreased. Regarding the hydrogen content, it was observed that it decreased in each cycle. During low-temperature catalytic steam gasification, it was observed that the amount of carbon monoxide could be significantly reduced starting from the 5^{th} regeneration cycle, while the amount of carbon dioxide could be significantly reduced in each of the regeneration cycles. Regarding the hydrogen content, an increase was achieved in each regeneration cycle. During high-temperature catalytic gasification (without steam), it was found that the amount of carbon dioxide could be significantly reduced, while the CO content could be increased until the 3^{rd} regeneration cycle. The hydrogen content showed a slight decrease. During high-temperature steam catalytic gasification, it was observed that the carbon dioxide content increased as the regeneration cycles progressed, while the CO content increased until the 7^{th} regeneration cycle. The hydrogen content showed decreasing values in the presence of the Ni/Clinoptilolite. The decreasing

carbon dioxide content and increasing CO content can be explained by the catalyst's high quadrupole moment and acidity.

d) It was determined that at temperatures of 400°C in the first reactor zone and 700°C in the second reactor zone without the use of steam, the amount of carbon dioxide was reduced by Ni/CaO until the third regeneration cycle. The amount of carbon monoxide was observed to decrease with the regeneration cycles. Regarding the hydrogen content, it was found that it decreased in each cycle relative to the relevant measurement points. During low-temperature catalytic steam gasification, it was observed that the content of carbon monoxide, carbon dioxide, and hydrogen was significantly reduced in each cycle. During high-temperature catalytic gasification (without steam), it was noted that the amounts of carbon dioxide and hydrogen could be significantly reduced as the regeneration cycles progressed, while the CO content could be increased until the 6^{th} regeneration cycle. During high-temperature catalytic steam gasification, it was demonstrated that the carbon dioxide content could be reduced until the 6^{th} regeneration cycle, and the carbon monoxide content showed a significant decrease depending on the regeneration cycles. The hydrogen content exhibited decreasing values in the presence of the applied catalysts. In the presence of the Ni/CaO catalyst, it was observed that the carbon dioxide content could mostly be significantly reduced, attributed to the carbon dioxide capture properties of CaO (especially when steam and low temperatures were applied). Additionally, an improvement in the efficiency of the carbon dioxide capture properties was observed, which can be explained by the catalyst's sintering when low temperatures were applied in the first reactor zone.

e) It was demonstrated that during low-temperature catalytic gasification (at a reactor zone temperature of 400°C), the syngas yield remained nearly constant in all regeneration cycles in the presence of the examined Ni/ZSM-5, Ni/Al_2O_3, and Ni/CaO. However, a significant increase in syngas yield was observed until the 6th regeneration cycle in the presence of Ni/Clinoptilolite. In the presence of the examined catalysts, the H_2/CO ratio varied between 0.06 and 0.36, while the CO/CO_2 ratio ranged from 0.7 to 1.3. It is important to note that the highest H_2/CO ratio was provided by the zeolite catalysts in all regeneration cycles.

f) It was determined that during low-temperature catalytic gasification (at a reactor zone temperature of 400°C) in the presence of steam, the syngas content remained nearly constant in the presence of Ni/Al_2O_3 and Ni/CaO, while the zeolite catalysts yielded outstanding values until the 6^{th} regeneration cycle. In the presence of the examined zeolite catalysts, the H_2/CO ratio varied between 0.01 and 0.15, while the CO/CO_2 ratio ranged from 1.2 to 1.9, the latter being suitable as a feedstock for methanol synthesis.

g) It was established that during high-temperature catalytic gasification (at a reactor zone temperature of 800°C) and in the presence of steam, the syngas content was slightly reduced until the 5th regeneration cycle and then significantly reduced by all examined catalysts. Additionally, in the presence of the catalysts, the H_2/CO ratio varied between 0.20 and 0.40, while the CO/CO_2 ratio ranged from 1.09 to 2.1.

Ranking the effectiveness of catalysts:

- Extent of average carbon dioxide reduction: Ni/Clinoptilolite > Ni/CaO > Ni/ZSM-5 > Ni/Al_2O_3
- Increase in average CO/CO_2 ratio: Ni/Clinoptilolite > Ni/ZSM-5 > Ni/CaO > Ni/Al_2O_3
- Increase in average H_2/CO ratio: Ni/Clinoptilolite > Ni/ZSM-5 > Ni/CaO > Ni/Al_2O_3
- Increase in average syngas yield: Ni/Clinoptilolite > Ni/CaO ~ Ni/Al_2O_3> Ni/ZSM-5
- Optimal syngas yield with suitable gas composition: Ni/Clinoptilolite ~ Ni/ZSM-5 > Ni/CaO ~ Ni/Al_2O_3

3.5. Gasification with post-situ adsorption

a) It was found that during the catalytic gasification at low temperature (first reactor zone temperature 400°C) in the presence of steam, the carbon monoxide content increased until the 5th regeneration cycle in the presence of Ni/ZSM-5, and then decreased, while that of with Ni/Clinoptilolite, a continuous increase was observed as a function of regeneration cycles. It was determined that using post-situ adsorption, the carbon dioxide content can be greatly reduced in the presence of the tested Ni/Clinoptilolite. In addition, the synthesis gas yield can be increased by nearly 50% in the presence of Ni/Clinoptilolite and by nearly 45% in the presence of Ni/ZSM-5 during high-temperature catalytic gasification in the presence of steam (800°C first reactor zone temperature).

b) It was determined that as the regeneration cycles progressed, the adsorbed carbon dioxide content decreases, where the main reason was the successive heat load during the regeneration (400°C) of the adsorbent, which caused transformation in the adsorbent structure, which resulted in a decrease in the efficiency of carbon dioxide adsorption. In addition, it was showed that in the presence of Clinoptilolite (placed as a post-situ adsorbent), the carbon dioxide content can be reduced by almost 50%, in addition, the carbon monoxide content can be increased by up to 20-60%, while the hydrogen content can be increased by 25-65%. It was found, that in case of post-situ adsorption, the synthesis gas yield in the first reactor zone

(400°C) can be increased by 68-160% on average, while at high temperature (800°C) it can be increased by 9.7-53.0%.

c) It was showed, that with post-situ adsorbent in the process, as well as with the tested Ni/ZSM-5 and Ni/Clinoptilolite catalysts, the value of carbon dioxide emission can be reduced by 94-100% in each of the regeneration cycles.

4. INDUSTRIAL APPLICATION OF THE RESULTS

The achieved results are greatly contributed to the chemical and mechanical engineering design of the large laboratory scale, complex gasification reactor system as the aim of the project ID number 2019-1.3.1-KK-2019-00015, "Establishment of a circular economy-based sustainability competence center at the University of Pannonia ". The reactor system is suitable for the gasification of different types of biomass with a capacity of 0.8-2.0 kg/h, with or without steam, at a temperature range of 800-1000°C and a pressure range of 1-5 bar. In addition to the gasification and reforming reactors, the complex reactor system also includes adsorber-desorber, absorber-desorber units and chemical gasification unit. With this reactor system, it will be possible to test the gasification and product purification processes on an enlarged scale using real raw materials.

5. PUBLICATIONS RELATING TO THE TOPIC OF THE DOCTORAL THESIS

5.1. Publications forming the basis of the PhD thesis

Published paper in foreign language in a foreign journal:

1. **V. Zsinka**, B. L. Tarcsay, N. Miskolczi, (**2024**) Determination of kinetic and thermodynamic parameters of biomass gasification with TG-FTIR and regression model fitting. Energies, 17, 1875. https://doi.org/10.3390/en17081875
2. **V. Zsinka,** N. Miskolczi, (**2024**) Investigation of regeneration cycles with different catalysts on steam gasification of biomass. Journal of the Energy Institute 114, 101632. https://doi.org/10.1016/j.joei.2024.101632
3. **V. Zsinka**, Sz. Tomasek, N. Miskolczi, (**2023**) Feasibility and economic issues of biomass pyrolysis-gasification: the effect of moisture content of raw material. Chemical Engineering Transactions, Vol. 99, 73-78. 10.3303/CET2399013
4. **V. Zsinka**, N. Miskolczi, T. Juzsakova, M. Jakab, (**2022**) Pyrolysis-gasification of biomass using nickel modified catalysts: The effect of the catalyst regeneration on the product properties. Journal of the Energy Institute, Vol. 105, 16-24. https://doi.org/10.1016/j.joei.2022.08.003

International, foreign language conference presentation with full text:

1. **V. Zsinka**, N. Miskolczi, Investigation of regeneration cycles with different catalysts on steam gasification of biomass, 17th SDEWES, 06-10th of November, **2022**. Paphos, Cyprus

International conference presentation in a foreign language with abstract:

1. **V. Zsinka**, N. Miskolczi, Pyrolysis-gasification of waste biomass with post-situ carbon capture, 24th International Symposium on Analytical and Applied Pyrolysis (Pyro2024), 19-23 May, **2024** Beijing, China
2. **V. Zsinka**, Sz. Tomasek, N. Miskolczi, Feasibility and economic issues of biomass pyrolysis-gasification: the effect of moisture content of raw material, ICheaP 16, 21-24 May, **2023**. Naples, Italy
3. **V. Zsinka**, N. Miskolczi, Investigation of scale-up and sustainable aspects of biomass gasification for syngas production, iconBM, 5-8 June, **2022**. Naples, Italy
4. **V. Zsinka**, N. Miskolczi, Adsorption based CO_2 capture with diverse featured zeolites, 27th Joint Annual Conference of the Chinese Society of Chemical Science and Technology in the UK and Society of Chemical Industry's Chinese UK Reginal Group (CSCST-SCI), 11-12 September **2020**., Belfast, UK

Conference presentation in Hungarian with an abstract:

1. **V. Zsinka**, N. Miskolczi, Biomassza elgázosítása laboratóriumi berendezésben, XXVIII. Nemzetközi Vegyészkonferencia, Nagyvárad 27-29. October **2022**.
2. **V. Zsinka**, N. Miskolczi, Kinetic study of biomass degradation using the TGA-FTIR method, Műszaki Kémiai Napok, Veszprém, 26-28 April, **2022**.

5.2. Publications concerning the subject area of the PhD thesis

Published paper in foreign language in a foreign journal:

1. **V. Zsinka**, J. Bobek-Nagy, A. Egedy, N. Miskolczi, Sz. Tomasek, H. Yang, (**2022**) Techno-economical analysis of CO_2 capture from biomass-derived syngas. Chemical Engineering Transactions, Vol.92. https://doi.org/10.3303/CET2292078
2. N. Miskolczi, **V. Zsinka**, O, Tóth, Z, Eller, N. Gao, Q. Cui, J. Bobek, (**2020**) Co-pyrolysis- reforming of Biomass and Residues from Waste Polymer Pyrolysis for CO_2 Reduction and Syngas Enhancement, Chemical Engineering Transactions, 81, 1195-1200. https://doi.org/10.3303/CET2081200
3. B.Fekhar, **V.Zsinka**, N.Miskolczi, (**2020**) Thermo-catalytic co-pyrolysis of waste plastic and paper in batch and tubular reactors for in-situ product improvement. Journal of EnvironmentalManagement, 269, 110741. https://doi.org/10.1016/j.jenvman.2020.110741
4. B. Fekhar, **V. Zsinka**, N. Miskolczi, (**2019**) Value added hydrocarbons obtained by pyrolysis of contaminated waste plastics in horizontal tubular reactor: in situ upgrading of the products by chlorine capture. Journal of Cleaner Production, Volume 241, 118116. https://doi.org/10.1016/j.jclepro.2019.118166
5. B. Fekhar, **V. Zsinka**, N. Miskolczi, (**2019**) Fuels by chemical recycling of waste plastic and biomass mixture and utilization of the products, Chemical Engineering Transactions, Volume 76, 1447-1452, https://doi.org/10.3303/CET1976242

Published paper in Hungarian in a Hungarian journal:

1. **Zsinka V.,** Nagy N. L., Miskolczi N., (**2020**) Műanyag-kompozitok és szintézisgáz előállítása Tetra Pak hulladékok újrahasznosításával, Polimerek VI. szám

International, foreign language conference presentation with abstract:

1. **V. Zsinka**, N. Miskolczi, Thermo-catalytic recycling of WEEE in one stage and two stage reactors FRPM **2021**.08.29-09. 01., Budapest
2. B. Fekhar, **V. Zsinka**, N. Gao, C. Quan, J. Sója, N. Miskolczi, Thermo-catalytic pyrolysis of waste plastics and biomass mixtures using Ni/ZSM-5 and Ni/SAPO-11 based catalysts: a kinetic approach, 6th International Conference on Biomass Energy (ICBE 2018), Wuhan, China, October 16- 19, **2018**
3. J. Sója, N. Miskolczi, **V. Zsinka**, 6th International Symposium on Gasification and its Application, Chengdu, China Valuable Gas and Liquid Hydrocarbon Products from Plastics Waste Pyrolysis over Different Modified Y-zeolite Catalysts, October 25-28, **2018**

Conference presentation in Hungarian with an abstract:

1. **Zsinka V**., Miskolczi N., Production of hydrogen/synthesis gas by catalytic pyrolysis reforming of multi-component polymer wastes from the packaging industry, XIV. Környezetvédelmi Analitikai és Technológiai Konferencia és 62. Magyar Spektrokémiai Vándorgyűlés, Balatonszárszó, SDG Családi Hotel és Konferencia-központ, **2019**. november 11-13.
2. M. Al-asadi, Miskolczi N., **Zsinka V.**, High temperature pyrolysis of real wastes polymers for hydrogen rich syngas production, Műszaki Kémiai Napok, Veszprém, **2019**. április 16-18.
3. **Zsinka V.**, Fekhar B., Miskolczi N., Low-temperature thermocatalytic thermal decomposition of waste polymers: in-situ quality improvement of products, XXIV. Nemzetközi Vegyészkonferencia, október 24-27., Szovátafürdő, Románia, **2018**

6. SCIENTIMETRIC DATA

The number of publications forming the basis of the PhD thesis:	**4**
cumulative impact factor:	**14,3**
The number of other publications concerning the subject area of the PhD thesis	**6**
cumulative impact factor:	**14,035**

Journal articles:

- a peer-reviewed publication in a foreign language, published in a foreign journal:	**9**
- a peer-reviewed publication, published in a Hungarian journal:	**1**

Papers published in conference publications:

- article in a foreign language published in an international conference publication:	1
- foreign language abstract published in an international conference publication:	6
- Hungarian abstract published in a Hungarian conference publication:	5

Number of all publications:	**10**
Summarized impact factor:	**28,335**
Number of independent references (based on Scopus):	**94**
h-index:	**4**

Veszprém, 2nd of September 2024.