

AN OVERVIEW OF PYROLYSIS CAPABILITIES OF MESOPOROUS CATALYSTS

Assist. Prof. Dr. Rahmiye Zerrin Yarbay-Şahin^{1,2*}

¹Bilecik Şeyh Edebali University Chemical Engineering Department, Bilecik, Turkey

² Bilecik Şeyh Edebali University, Energy Technologies Application and Research Centre
Bilecik, Turkey

(ORCID: 0000-0002-4926-044X)

zerrin.yarbay@bilecik.edu.tr

ÖZET

Temiz ve yenilenebilir enerji talebi, fosil yakıtların hızla tükenmesi ve sıkı çevresel ve politik kısıtlamalar nedeniyle artmaktadır. Bu durumda biyokütle, yalnızca temiz bir enerji taşıyıcısı olmakla kalmayıp aynı zamanda daha az karbon salınımlı bir toplumun nihai hedefini temsil eden doğal bir seçenek olarak ortaya çıkmaktadır. Çeşitli termokimyasal dönüşüm işlemleri arasında, piroliz bio-oil üretimi için tercih edilir. Dönüşüm işlemlerinin optimizasyonu, çeşitli katalitik sistemler uygulanarak gerçekleştirilebilmektedir. Bu amaçla kullanılan yöntemlerden biri, biyokütle piroliz bio-oilinin çeşitli katalizörler kullanılarak iyileştirilmesidir. Literatüre göre, kullanılan katalizörler arasında HZSM-5'in bio-oilin parçalanması veya dönüştürülmesi için en etkili katalizör olduğu bilinmektedir. HZSM-5'in bu mükemmel performansı, şekil seçiciliği, iyon değişim kapasitesi ve benzersiz asit özellikleri ile ilişkilendirilmiştir. Diğer taraftan, mikro gözenekli HZSM-5, özellikle büyük moleküller için düşük kütle aktarım hızları ile dezavantajlıdır.

Bu derleme çalışmasında, literatürde katalitik pirolizde kullanılan Al-SBA-15, Al-MCM-41, mezogözenekli alüminosilikat malzemeler (MSU-SBEA), mordenit çerçeve ters çevrilmiş (MFI) katalizörler ve hiyerarşik mezopoz Y (mezo Y) çalışmaları incelenmiştir. Katalitik performans ve ürünlerin bileşimi analiz edilerek değerlendirilmiştir. Piroliz ürün dağılımları ve bio-oilin analiz sonuçları derleme kapsamında incelenmiştir. Farklı ham maddelerin kullanılması ve farklı deney koşullarının uygulanması nedeniyle deneylerden elde edilen sonuçlar birbiriyle doğrudan karşılaştırılamasa da, bio-oil miktarı ve kalitesi ile ilgili tavsiyeler tartışmaya değerdir.

Anahtar Kelimeler: Piroliz; Bio-oil; Mezogözenekli katalizörler.

ABSTRACT

The demand for renewable energy is growing due to depletion of fossil fuels and environmental and political regulations. According to this, biomass is emerging as a natural choice due to not only being a clean energy carrier but also representing the final objective of a decarbonized society. Between the thermochemical conversion processes, pyrolysis is favoured for bio-oil production. In recent years, catalytic systems have been proposed as an encouraging way by realizing the upgrading of the biomass pyrolysis bio-oil using various catalysts. According to the literature, HZSM-5 is very well known to be the most effective catalyst for cracking or reforming bio-oil. This excellent performance of HZSM-5 has been related to the shape-selectivity, ion exchange capacity, and unique acid characteristics. On the other hand, HZSM-

5 with micropores is a disadvantage that is restricted by the low mass transfer rates, mainly for large molecules.

In this review, mesoporous materials including Al-SBA-15, Al-MCM-41, mesoporous aluminosilicate materials (MSU-SBEA), mordenite framework inverted (MFI) catalysts and hierarchical mesoporous Y (meso Y) as potential catalysts employed in catalytic pyrolysis in recent articles have been reviewed. The catalytic performance was assessed by analysing the composition of the products. Pyrolysis product distributions of pyrolysis and properties of bio-oil have dealt. Although the results from the experiments cannot be directly compared with each other due to the using different raw materials and applying different experimental conditions, recommendations on bio-oil quantity and quality are worth to discuss.

Keywords: Pyrolysis; Bio-oil; Mesoporous catalysts.

1. INTRODUCTION

Pyrolysis is an appealing process which can convert biomass into valuable liquid product called bio-oil, which is achieved by the varied heating rates, residence times, and temperatures especially in the absence of oxygen [1]. Bio-oil is a mixture of many compounds including hydrocarbons, oxygenated species such as organic acids, (dehydrated) carbohydrates, aldehydes, ketones, (depolymerized) lignin fragments, etc. [2]. Catalytic pyrolysis, is preferred in order to develop reactions namely cracking, decarbonylation, decarboxylation, deoxygenation, etc., for better the bio-oil quality while enhancing valuable compound amounts [1].

Up to now, many researchers studied about catalytic pyrolysis of biomass converting into bio-oil using different catalysts. Most of them worked on understanding the catalytic pyrolysis of biomass to attain the valuable bio-oil with typical catalysts such as zeolite catalysts [1, 3, 4]. However, zeolites exhibit a problem when large reactant molecules were considered, particularly in liquid-phase systems as is commonly the case in the preparation of fine chemicals, related to the fact that mass transfer limitations are very severe for microporous solids. Efforts to recover the diffusion of reactants to the catalytic sites have so far dealt with growing the pore sizes, on reducing crystal size, or on obtaining an additional mesopore system [5].

As the ordered mesoporous silicas like MCM-41 and SBA-15 discovered in the 1990s, mesoporous materials have gained attention because of their wide range of applications [6]. The introduction of porous materials in several industrial processes has brought important economic and environmental benefits. These benefits have attracted the many research group's attention related to preparation of these materials with novel framework topologies and pore architecture [7].

2. REVIEWING CATALYST EFFECT

According to the literature, it can be highlighted that in many studies related to mesoporous catalyst used in pyrolysis, the pyrolysis characteristics and products distribution were examined prominently [8-15]. Besides, compounds in the bio-oil were analysed with some spectroscopic techniques including GC, GC/MS, TGA, etc. in detail. The studies selected from the literature is investigated in terms of biomass conversion and bio-oil properties, separately.

2.1. CATALYST EFFECT ON BIOMASS CONVERSION

Adam et al. examined the performances of Al-MCM-41 type catalysts, Fluid Catalytic Cracking (FCC) catalyst, SBA-15 and an Al-SBA-15 catalyst for pyrolysis of spruce wood vapours at 500 °C and reported that while an increment in gas yield and aqueous part in the liquid phase was observed in each catalytic experiment, the coke yield remained the same or slightly decreased compared to the non-catalytic experiments. Surprisingly, they recorded that the biomass type did not seem to have a significant influence on the desirable and undesirable product yields in their catalytic pyrolysis results mesoporous catalysts involved [8]. Özbay et al. studied catalytic pyrolysis of banana peel at 550 °C at 7 °C/min for 20 min under atmosphere with Al-SBA-15 catalyst. According to their results, Al-SBA-15 was able to catalysing of banana peel biomass resulting in bio-oil yields of 18–28% with varying catalyst/biomass ratios (0- 20 wt%). The highest bio-oil yield from the catalytic pyrolysis was 18.64% with 15 wt% catalyst/biomass ratios [9]. Another interesting study was conducted by Park et al. They dealt with catalytic upgrading of pyrolytic vapours obtained from radiata pine sawdust using mesoporous MFI. The catalytic activity was compared with conventional HZSM-5 and mesoporous material from HZSM-5. Mesoporous MFI gave the highest activities regarding deoxygenation and aromatization, during the catalytic upgrading of pyrolytic vapours due to the synergic effect of its high porosity and acidity. In addition, mesoporous MFI reduced both the organic fraction and bio-oil yield [10]. In the study of Gamliel et al., cellulose and miscanthus was pyrolyzed using pyrolysis gas chromatography system (PyGC) with mordenite framework inverted (MFI) zeolites. Their results indicated that higher amount of mesopore volume was required for optimal acid site accessibility leading to better bio-oil yield. When obtained, intermediate aromatic hydrocarbons were remained to polymerize to form bulky polycyclic aromatic hydrocarbons (PAHs) and coke [11].

2.2. CATALYST EFFECT ON BIO-OIL PROPERTIES

According to the study conducted by Adam et al., Al-MCM-41 and SBA-15 materials were experienced for converting pyrolysis vapours of spruce wood. The results showed that the hydrocarbon and phenol yields improved, while the carbonyl and the acid yields declined in the catalytic experiments [8]. Rezaei et al. investigated catalytic co-pyrolysis of yellow poplar (YP) and high-density polyethylene (HDPE) over mesoporous solid catalysts including hierarchical mesoporous MFI, hierarchical mesoporous Y and Al-SBA-15. The production yields of aromatic hydrocarbons obtained from the catalytic co-pyrolysis YP and HDPE mixture having different mixing ratio of HDPE (0, 25, 50, 75, and 100%) of the mixtures over the catalysts were compared using a tandem micro reactor-gas chromatography/mass spectrometry (TMR-GC/MS). According to their results, Meso-MFI used run of YP provided high aromatic hydrocarbon harvest. High aromatization was found to be related to MFI catalyst pore structure with large pore size and strong acidity [12]. The in-situ upgrading of biomass pyrolysis vapours with mesoporous aluminosilicate materials (MSU-SBEA) assembled from zeolite Beta (BEA) seeds was evaluated by Triantafyllidi et al., in comparison to conventional Al-MCM-41 and to non-catalytic biomass pyrolysis conducted at 500 °C. MSU-S usage caused lower organic phase content in the bio-oil besides entailing higher coke and char yields, compared to non-catalytic pyrolysis and to the use of Al-MCM-41 which induced a small increase in the yields of liquid oil and coke. The MSU-Ss were found to be selective towards PAHs and heavy fractions, while they formed negligible amounts of acids, alcohols and carbonyls, and very few phenols. The

MSU-S materials showed stronger acid sites than Al-MCM-41, resulting in enhanced yields of aromatics, PAHs and coke [13]. Jeon et al. examined SBA-15, Pt/SBA-15, AlSBA-15, and Pt/AlSBA-15 for cellulose, hemicellulose, and lignin pyrolysis. The catalytic performances of their AlSBA-15 and Pt/AlSBA-15 catalyst was found to be superior to SBA-15 and Pt/SBA-15. Pt/AlSBA-15 usage led to produce higher amounts of furans and aromatics. The catalytic upgrading of products of hemicellulose similarly enhanced the of furan, ethanol, and aromatics yields which improve the bio-oil quality. However, an increment in production of acids both for cellulose and hemicellulose were observed. Catalytic pyrolysis of lignin improved phenolics production, particularly, with less amount of carbonyl group [14]. Kim et al. investigated the pyrolysis of citrus peels biomass' by TGA, evolved gas analysis–mass spectrometry and TMR-GC/MS analyses. Mesoporous MFI was reported to be a more effective catalyst for the production of mono aromatic compounds and light olefins than Al-MCM-41 related to its higher catalytic activity in deoxygenation and aromatization due to their stronger acidities [15].

3. CONCLUSION

Environmental and economic considerations have gained attention to redesign commercially significant processes so that the usage of harmful constituents and the generation of toxic waste could be avoided. In this regard, heterogeneous catalysis shows a key role in the progress of environmentally well-natured processes. Mesoporous catalysts permit larger molecules to pass through the pore, to be processed there and to leave the pore system again effectively.

From the literature, the following points were noted:

- The catalyst application for pyrolysis of bio-oil is very important for the future of biofuels.
- The mesoporous catalyst showed an impressive potential to increase the bio-oil yield in many works. Also, mesoporous catalysts were found to increase the amount of desirable products more than undesirable products.
- In many studies, higher catalytic activity in deoxygenation and aromatization was found to due to the large pore size and stronger acidity of mesoporous catalysts used.
- One of the mesoporous catalyst's drawback was found as the PAH formation. New investigation in this area is compulsory and welcome.

REFERENCES

1. Wang, W., Li, X., Ye, D., Cai, L., & Shi, S. Q. (2018). Catalytic pyrolysis of larch sawdust for phenol-rich bio-oil using different catalysts. *Renewable Energy*, 121, 146-152.
2. Venderbosch, R. H. (2015). A critical view on catalytic pyrolysis of biomass. *ChemSusChem*, 8(8), 1306-1316.
3. Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., & Murzin, D. Y. (2008). Catalytic pyrolysis of woody biomass in a fluidized bed reactor: influence of the zeolite structure. *Fuel*, 87(12), 2493-2501.
4. Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., & Murzin, D. Y. (2007). Catalytic pyrolysis of biomass in a fluidized bed reactor: influence of the acidity of H-beta zeolite. *Process Safety and Environmental Protection*, 85(5), 473-480.
5. Taguchi, A., & Schüth, F. (2005). Ordered mesoporous materials in catalysis. *Microporous and mesoporous materials*, 77(1), 1-45.

6. Ren, Y., Ma, Z., & Bruce, P. G. (2012). Ordered mesoporous metal oxides: synthesis and applications. *Chemical Society Reviews*, 41(14), 4909-4927.
7. Perego, C., & Millini, R. (2013). Porous materials in catalysis: challenges for mesoporous materials. *Chemical Society Reviews*, 42(9), 3956-3976.
8. Adam, J., Antonakou, E., Lappas, A., Stöcker, M., Nilsen, M. H., Bouzga, A., ... & Øye, G. (2006). In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials. *Microporous and Mesoporous Materials*, 96(1-3), 93-101.
9. Ozbay, N., Yargic, A. S., Sahin, R. Z. Y., & Yaman, E. (2019). Valorization of banana peel waste via in-situ catalytic pyrolysis using Al-Modified SBA-15. *Renewable energy*, 140, 633-646.
10. Park, H. J., Heo, H. S., Jeon, J. K., Kim, J., Ryoo, R., Jeong, K. E., & Park, Y. K. (2010). Highly valuable chemicals production from catalytic upgrading of radiata pine sawdust-derived pyrolytic vapors over mesoporous MFI zeolites. *Applied Catalysis B: Environmental*, 95(3-4), 365-373.
11. Gamliel, D. P., Cho, H. J., Fan, W., & Valla, J. A. (2016). On the effectiveness of tailored mesoporous MFI zeolites for biomass catalytic fast pyrolysis. *Applied Catalysis A: General*, 522, 109-119.
12. Rezaei, P. S., Oh, D., Hong, Y., Kim, Y. M., Jae, J., Jung, S. C., ... & Park, Y. K. (2017). In-situ catalytic co-pyrolysis of yellow poplar and high-density polyethylene over mesoporous catalysts. *Energy Conversion and Management*, 151, 116-122.
13. Triantafyllidis, K. S., Iliopoulou, E. F., Antonakou, E. V., Lappas, A. A., Wang, H., & Pinnavaia, T. J. (2007). Hydrothermally stable mesoporous aluminosilicates (MSU-S) assembled from zeolite seeds as catalysts for biomass pyrolysis. *Microporous and Mesoporous Materials*, 99(1-2), 132-139.
14. Jeon, M. J., Jeon, J. K., Suh, D. J., Park, S. H., Sa, Y. J., Joo, S. H., & Park, Y. K. (2013). Catalytic pyrolysis of biomass components over mesoporous catalysts using Py-GC/MS. *Catalysis Today*, 204, 170-178.
15. Kim, Y. M., Jae, J., Lee, H. W., Han, T. U., Lee, H., Park, S. H., ... & Park, Y. K. (2016). Ex-situ catalytic pyrolysis of citrus fruit peels over mesoporous MFI and Al-MCM-41. *Energy Conversion and Management*, 125, 277-289.