Catalyx : Journal of Process Chemistry and Technology
Volume. 1 Issue 1 July 2024
Page No: 18-32

In-situ and Co-pyrolysis of Empty Fruit Bunch Fiber for Hydrocarbon Production

Bashar Hadi Abdullahi[1] , Abdullahi Muhammad Sokoto[2], Aminu Bayawa Muhammad[3], Yahaya Alhassan[4] and Chika Muhammad[5]
Shehu Shagari College of Education, Sokoto Nigeria[1]
Usmanu Danfodiyo University, Sokoto Nigeria[2,3,5]
Federal University, Gusau Nigeria[4]
Correspondent: alkanci123@gmail.com [1]

Received : May 23, 2024
Accepted : Juny 25, 2024
Published : July 15, 2024

Citation: Abdullahi, B, H., Sokoto, A, M., Muhammmad, A, B., Alhassan, Y., & Muhammad, C. (2024). In-situ and Co-pyrolysis of Empty Fruit Bunch Fiber for Hydrocarbon Production. Catalyx : Journal of Process Chemistry and Technology, 1(1), 18-32

ABSTRACT: Significant amount of empty oil palm bunches are produced annually in Nigeria that mostly going to waste or as animal feed. This study explores the feasibility of transforming these bunches into hydrocarbons via pyrolysis process. The MoO3 and NiO catalyst materials facilitated the catalytic pyrolysis resulting in favourable properties of EFB fibre pyrolysis products suitable for various applications. Valuable compounds were identified through GC-MS analysis of pyrolysis oils. In-situ catalytic pyrolysis with MoO3 and NiO catalysts favored acidic compounds, and produced combustible (CH4) and non-combustible (CO2) gases. Co-pyrolysis of Low-Density Polyethylene and the fiber generated high olefins and paraffin production, along with a significant 40% methane gas yield in both processes. The study highlights the conversion potential of agricultural waste into valuable hydrocarbons, emphasizing the crucial role of catalysts with selectivity for acidic compounds and achieving high olefin, paraffin, and up to 40% methane gas yields in both co-pyrolysis and catalytic pyrolysis process.

Keywords: Co-pyrolysis, In-situ Pyrolysis, EFB, Nickel oxide, Molybdenum oxide

INTRODUCTION

Palm oil production has witnessed a remarkable surge in recent years, with Nigeria boasting the world's second-largest palm oil plantation area (Kilby, 1967). This expansion has translated into a substantial rise in palm oil waste, including empty fruit bunch (EFB) fiber. EFB fiber, a lignocellulosic biomass, is conventionally employed as fuel for generating energy or incinerated to obtain fertilizer. However, this waste material holds immense potential for conversion into sustainable energy if utilized effectively(Kimia et al., 2017).

During the palm oil mill production process, approximately 14% of mesocarp fiber (MF), 7% of palm kernel shell (PKS), and 23% of empty fruit bunch (EFB) fiber are generated annually. As cited by Yang et al. (Won, 2016), EFB fiber contributes to a staggering 19.5 million tons of solid waste produced each year. Nigeria is experiencing rapid growth in palm oil production, and while

this brings significant economic benefits, it also results in the generation of a massive amount of EFB waste, posing a significant environmental threat(Otti et al., 2014). Improper disposal of these agricultural residues generated during and after farming activities can lead to severe environmental hazards (Salman et al., 2019).

Traditionally, EFB fiber waste has been utilized as fuel to generate energy or burned in incinerators to produce fertilizer [1]. However, this waste material holds immense potential for conversion into sustainable energy sources if harnessed effectively (Yoo et al., 2019). Pyrolysis, a thermochemical conversion technique, transforms suitable substrates into three distinct products: solid char, pyrolysis oil, and gaseous products (Dutta & Pal, 2014; Sukiran et al., 2014; J. Zhang et al., 2010). These products can be directly utilized or further upgraded to produce fuels and petrochemical hydrocarbons.

Despite its energy content and diverse organic compounds, pyrolysis oil suffers from several inherent drawbacks, including acidity, oxygenated compounds, and high water content, rendering it unsuitable for direct use as a fuel (Demirbas, 2009). To achieve fuel-grade quality, pyrolysis oil must undergo further treatments or catalytic upgrades (Bajus, 2010; Mukarakate, 2014).

Enhancing pyrolysis oil quality and alleviating upgrade challenges necessitates the employment of catalytic pyrolysis (Lindfors, 2019). This process improves the bio-oil refining process by employing either ex-situ catalysis, involving catalytic cracking, hydrodeoxygenation, and esterification processes, or in-situ catalytic pyrolysis, a promising thermochemical conversion route that produces chemicals and fuels compatible with existing petrochemical infrastructure (Dickerson & Soria, 2013). Developing robust and highly selective catalysts is crucial for the advancement of catalytic pyrolysis . These catalysts play a pivotal role in transforming pyrolysis oil into a viable and sustainable fuel source.

The deoxygenation upgrade process of bio-oil, a crucial step in pyrolysis oil refinement, presents significant challenges. Removing the aryl-oxygen bond in the oxygenated compounds of pyrolysis oil proves to be a formidable task (Barrett, 2016). The process continues to face hurdles such as coke deposition and catalytic deactivation, necessitating the development of innovative catalysts, methods, and chemical approaches (Lindfors, 2009).

The complexities of deoxygenation stem from the stability of the aryl-oxygen bond, demanding more potent catalysts and reaction conditions to break this bond effectively . Coke deposition, the accumulation of carbonaceous residues on the catalyst surface, impedes the catalytic activity and reduces the overall efficiency of the deoxygenation process. Furthermore, catalytic deactivation, the loss of catalytic activity over time, poses another challenge, necessitating the development of robust and durable catalysts that can withstand the harsh reaction conditions. The development of effective and efficient deoxygenation technologies is crucial for the advancement of biofuel production and the transition to a more sustainable energy future.

Numerous researchers have demonstrated that catalytic in-situ pyrolysis enhances the carbon output of petrochemicals and reduces coke formation by introducing appropriate catalysts in the correct proportions(Panda & Singh, 2011). Nickel-oxide catalysts supported on SiO_2 and γ-Al_2O_3 have been successfully employed to investigate the hydrodeoxygenation of stearic acid using n-

dodecane as a solvent at temperatures ranging from 533 to 563 K, yielding n-Pentadecane, n-hexadecane, n-heptadecane, n-octadecane, and l-octadecanol as products [21]. In addition, thermal degradation studies of palm oil empty fruit bunch fibre (EFBF) in the presence of CaO, MgO, and ZnO in-situ catalysts have reported improved bio-oil characteristics(Lødeng, 2017). The incorporation of these oxides lowers the average activation energy (Chong et al., 2019; Idris et al., 2020; Sharma et al., 2015). Consequently, research has identified catalysts as playing crucial roles, with zeolites and specific oxide-based catalysts being commonly utilized in the process (Krutof, 2018).

Various studies have concurred that co-pyrolysis technology holds the potential to significantly enhance the quantity and quality of pyrolysis oil without necessarily requiring the addition of catalysts, solvents, or free hydrogen pressure (B. Zhang et al., 2015). Many researchers also view it as a rapid, cost-effective, and efficient method for transforming waste materials into high-quality biofuels. Mlynková et al. (Mlynková et al., 2008) reported that the co-pyrolysis process of biomass-plastic mixtures effectively converts waste materials into valuable products such as aromatic compounds and reduces coke deposition during the process. The availability of waste materials for co-pyrolysis could play a significant role in the sustainability of this technology for the production of high-quality biofuels and contribute to environmentally friendly waste plastic disposal (Vuthaluru, 2004a). Idris et al. achieved high yields of aromatic compounds from the catalytic co-pyrolysis of corn stalks with high-density polyethylene (HDPE) using an HZSM-5 zeolite catalyst at temperatures ranging from 500°C to 600°C (Idris, 2021).

Similarly, microwave-assisted optimization studies of EFB fiber and waste truck-tire (TT) co-pyrolysis revealed an optimal temperature of around 505°C, yielding an olefin-rich oil (39.0%) [23]. Conversely, Xue et al. reported an optimal temperature of 625°C for the co-pyrolysis of red oak with LDPE. Xue et al. (Xue et al., 2015) observed that the biochar obtained from HDPE and red oak co-pyrolysis exhibited a larger BET surface area than pure red oak biochar. This is attributed to the synergistic interaction that resulted in the formation of large and shallow micropores on the char surface. Consequently, further treatment could produce high surface area activated carbon from the carbonaceous pyrolysis char product. Therefore, diesel-like hydrocarbons can be produced from both catalytic and thermal co-pyrolysis processes.

The gaseous fraction from pyrolysis, which can be burned to provide the energy required for the pyrolysis process, is highly dependent on the operating conditions employed during pyrolysis. However, excessive heat transfer can lead to further cracking of primary volatiles into gaseous products [30](Wong et al., 2015). In-situ catalytic pyrolysis with Molybdenum oxide (MoO3) and Nickel oxide (NiO) was investigated for their potential to improve pyrolysis oil quality at a pyrolysis temperature of 500°C. Similarly, the co-pyrolysis process of fiber with Low-density Polyethylene (LDPE) was studied.

The research tries to answer the following research questions:

1. How can Empty Fruit Bunch (EFB) fiber, a significant byproduct of palm oil production, be effectively utilized for sustainable energy generation?

2. What are the potential benefits and challenges associated with in-situ and co-pyrolysis processes for converting EFB fiber into hydrocarbons as energy sources?
3. What are the characteristics of the pyrolysis products obtained from EFB fiber, including pyrolysis oils and gaseous fractions, and how do they compare between in-situ and co-pyrolysis approaches?
4. What are the key factors influencing the quality and composition of pyrolysis oils derived from EFB fiber, and how can catalytic upgrading processes address inherent drawbacks such as acidity and high water content?
5. How do different catalysts, reaction conditions, and process parameters affect the efficiency and selectivity of deoxygenation reactions during the upgrading of pyrolysis oils from EFB fiber?

The aim of this research is to investigate the performance of NiO and MoO3 catalysts in the conversion of Oil Palm Empty Fruit Bunch (EFB) into hydrocarbons and set to be achieved through the following specific objectives:

1. To evaluate the potential of in-situ and co-pyrolysis processes for converting EFB fiber into hydrocarbons suitable for sustainable energy production.
2. To investigate the composition, characteristics, and thermal behavior of pyrolysis products obtained from EFB fiber using GC-MS analysis (gas chromatography).
3. To assess the effectiveness of catalytic upgrading techniques, such as in-situ catalytic pyrolysis, for improving the quality and usability of pyrolysis oils derived from EFB fiber.
4. To identify and optimize key parameters, including catalyst types, reaction temperatures, and residence times, to enhance the efficiency and selectivity of deoxygenation reactions during pyrolysis oil upgrading.
5. To explore the potential synergistic effects of co-pyrolysis processes involving EFB fiber and other feedstocks, such as low-density polyethylene (LDPE), in enhancing the yield and quality of pyrolysis products.

Conceptual Framework:

This framework explores two novel methods for extracting valuable hydrocarbons from EFB fiber for use as sustainable energy sources:

In-situ pyrolysis

EFB fibres undergo pyrolysis, or thermal degradation in the presence of catalysts (MoO3 and NiO oxides), at 500°C. These catalysts might encourage the production of desirable hydrocarbon molecules in the pyrolysis oil's organic fractions.

Co-pyrolysis

At 500°C, EFB fibres and Low-Density Polyethylene (LDPE) resins co-pyrolyze. By examining potential synergistic effects between EFB and LDPE during pyrolysis, this approach aims to increase the amount of hydrocarbons produced in the co-pyrolysis oil.

Non-condensable gas analysis

Monitoring of the gaseous products generated during the in-situ and co-pyrolysis processes will be done using a portable gas analyzer. This study will reveal both combustible (like CH4) and non-combustible gases, offering information about the process's possible fuel value.

Organic fraction analysis (GC-MS)

The pyrolysis oils of organic components was characterised using gas chromatography-mass spectrometry (GC-MS) identify and quantify the hydrocarbon molecules generated by each pyrolysis technique will be determined.

METHOD

Palm oil EFB fiber samples collected from three different palm oil processing plants (Otukpa, Oroken, and Owukpa) in Benue State, Nigeria, were kept in an airtight container until required for analyses. After that, the sample was pretreated with distilled water three times. Then it was dried for 24 hours at 105°C in an oven and stored in polythene bags. Similarly, low-density polyethylene (LDPE) plastics resin was procured from NILEST, Zaria. The sample was kept in an airtight container until required for analysis.

1. Preparation and Characterization of MoO3 and NiO Oxide Catalysts

A molybdenum oxide catalyst was prepared through a hydrothermal process. Ten grams of ammonium heptamolybdate tetrahydrate (NH4)6Mo7O24.4H2O) (MOLYCHEM) in 20 ml of distilled water. Then it was allowed to dissolve wholly for 1hr. Then the solution formed was oven dried at 105°C and then calcined at 400°C for 4hrs (L. Barrientos, 2009; Wang, 2020). Equally, for nickel oxide catalyst material, 10g of Nickel nitrate hexahydrate(Ni(NO3)2.6H2O (MOLYCHEM) was measured and dissolved in 20 ml of distilled water. Then the solution formed was oven dried at 105°C and then calcined at 550°C for 6hrs (Kumar et al., 2014; Sharma et al., 2015).

2. Thermal Pyrolysis Process

A Pyrex reactor with an outlet tube at one end (145 mm long with an inner diameter of 37 mm and an outer diameter of 41 mm) was used in conjunction with a tubular furnace and temperature control system to perform the thermal pyrolysis process. The temperature of the furnace was regulated using a PID (proportional-integral-derivative) controller with an accuracy of 0.3%. The reactor was heated externally and equipped with Cr-Al: K type thermocouples installed within the reactor to monitor the temperature. Hadi et al. used a similar setup for their pyrolysis experiments. During the process, 5g of the sample was transferred into a Pyrex glass reactor column and flushed with nitrogen gas for 10 minutes before the pyrolysis began. The process was conducted in an inert environment with a steady nitrogen gas supply at standard atmospheric pressure. In the end, condensable fractions were collected using a cylinder, and then the organic fraction of the liquid products was placed in a sterile sample vial for analysis (Hadi et al., 2017; Muhammad et al., 2021).

3. In-situ Catalytic and Co-pyrolysis Process

The in-situ and co-pyrolysis processes were conducted in the same Pyrex glass reactor used for the thermal pyrolysis process. For the in-situ catalytic pyrolysis process, 5g of EFB sample was mixed with either 5wt% or 15wt% of NiO catalyst. For the in-situ catalytic pyrolysis process, 5g of EFB sample was mixed with 10wt% or 15wt% of MoO3 catalyst. The co-pyrolysis process of EFB fiber with LDPE resin was carried out using various ratios (100% EFB, 10% LDPE & 90% EFB, 20% LDPE & 80% EFB, 40% LDPE & 60% EFB) and then pyrolyzed with EFB using the Pyrex glass reactor as in the thermal pyrolysis procedure.

The organic fractions of the pyrolysis oil from both co-pyrolysis and in-situ catalytic pyrolysis processes were subjected to GC-MS analysis at the Central Advance Science Laboratory Complex (CASLaC) of Usmanu Danfodiyo University, Sokoto, to determine the chemical composition of the organic fraction obtained from the liquid products. Similarly, the gaseous products collected using a gas collector were analyzed at Sokoto Energy Research Center using a portable hand gas analyzer (Shenzhen Energy Co. Ltd with an accuracy of CH4 & CO2 <2%).

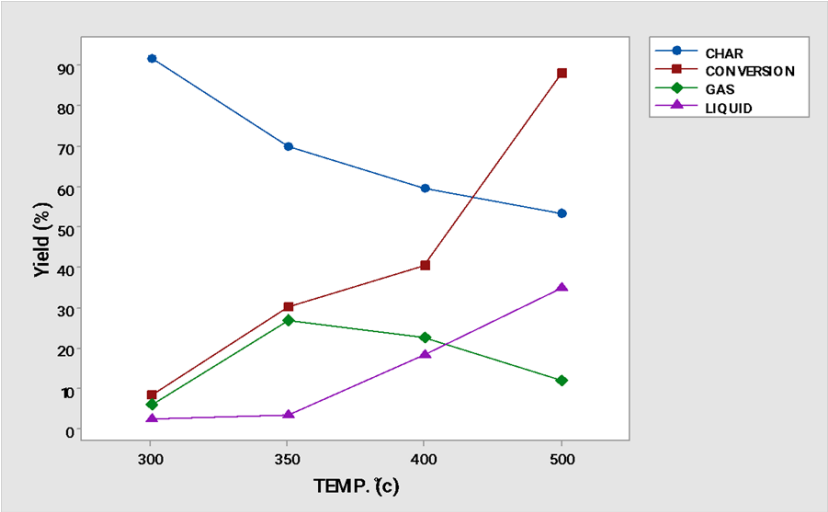
Additionally, the surface area and pore volume analysis of the co-pyrolysis solid residue (char) were determined. The surface area and pore volume of activated carbon (AC) were determined using N_2 adsorption isotherms at 77.35K using Quantachrome Instrument (Version 11.03). The surface area was determined using the Brunauer-Emmett-Teller (BET) method. Concurrently, pore volume and pore size were estimated through the application of the Barrett-Joyner-Halenda (BJH) method. The Dubinin-Radushkevich (DR) method was employed to determine the micropore surface area (Collin et al., 2015).

RESULT AND DISCUSSION

1. Effect of Temperature on Mass Balance of EFB Fiber Thermal Pyrolysis

Figure 1 demonstrates that temperature has major effect on the fiber's pyrolysis. At 500°C, the yield of liquid product was highest (34.64%) while the yield of residue was lowest (53.46%). The results are in line with those of Sukiran et al. (Sukiran et al., 2009), who also noted that the ideal yield for EFB fibre was reached at 500°C. Comparably, it agrees with the findings of Idris et al. (Patel et al., 2013) regarding the pyrolysis of Malaysian EFB fibre, where 442.15°C was shown to be the ideal temperature. At 500°C, the highest percentage conversion (88.10%) and liquid product yield (34.64%) were also noted.

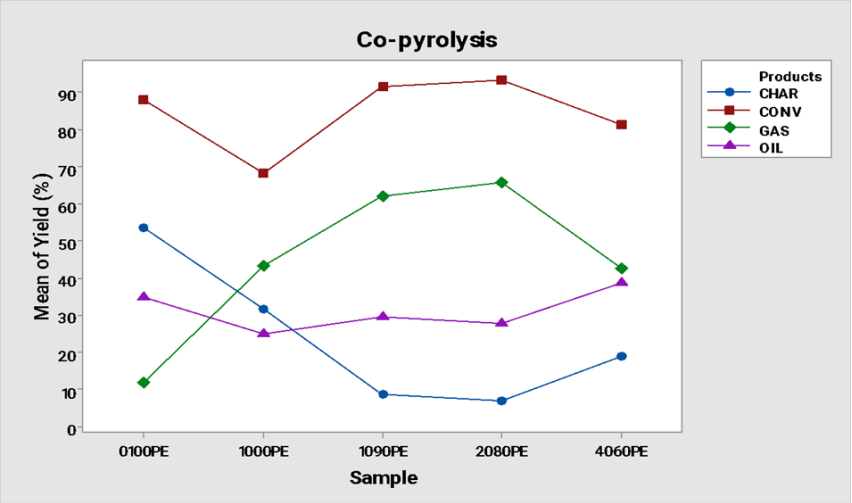
Figure 1: Effect of Pyrolysis Temperature on Mass Balance of Thermal Pyrolysis



2. Effect of Co-pyrolysis on the Yield of Products

Co-pyrolysis of fibre with plastic materials greatly improves the yield of hydrocarbons (olefins, naphthenic, and paraffin), according to numerous pyrolysis studies carried out to investigate the hydrocarbon potential of lignocellulosic substances. As a result, Figure 2's results demonstrate a high synergy between the plastic and fibre materials. Compared to the 2080PE mixture (6.6%), the yield of solid char (11.9%) from the 0100PE EFB mixture was found to be much lower. Nonetheless, it was noted that the 4060PE (31.74%) mixture produced a higher yield of solid product (char), which is explained by the need for high temperatures for the breakdown of plastic materials (Hazrat et al., 2014). Therefore, the liquid yield provided additional evidence of the anticipated effect of the plastic in the co-pyrolysis mixture.

Figure 2: Effect of Co-pyrolysis on the Product Yield at 500°C

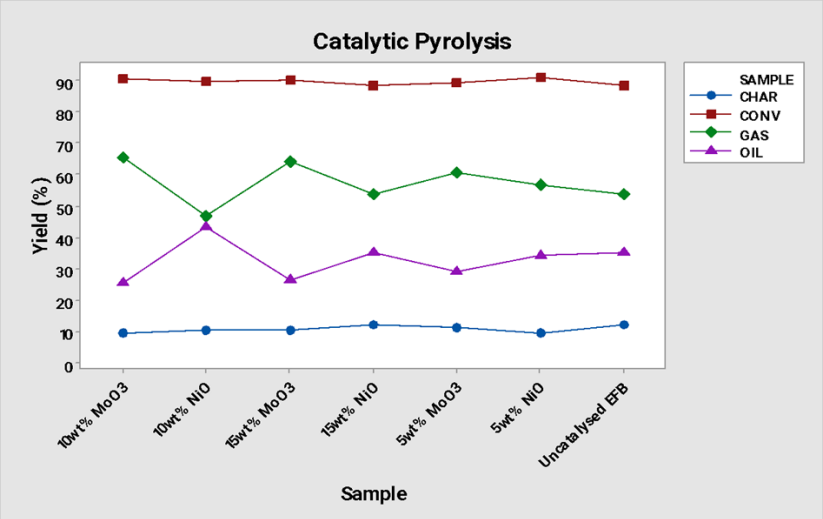


3. Effects of Catalysts on the Yield of Products

As seen in Figure 3, there was a significant difference ($P<0.005$) between the products of the pyrolysis of EFB that were catalysed and those that weren't. According to the results, both catalysts are selective in their activity rather than having any effect on the conversion process. With

10wt% NiO catalyst, the maximum yield of liquid product was obtained at 43.22%, whereas 10wt% MoO3 catalyst produced the highest gaseous product at 65.29 percent. The significant gaseous output observed may have arisen from the catalyst's assistance in the secondary cracking of compounds with higher molecular weight (Ayodele et al., 2014; López-González et al., 2013).

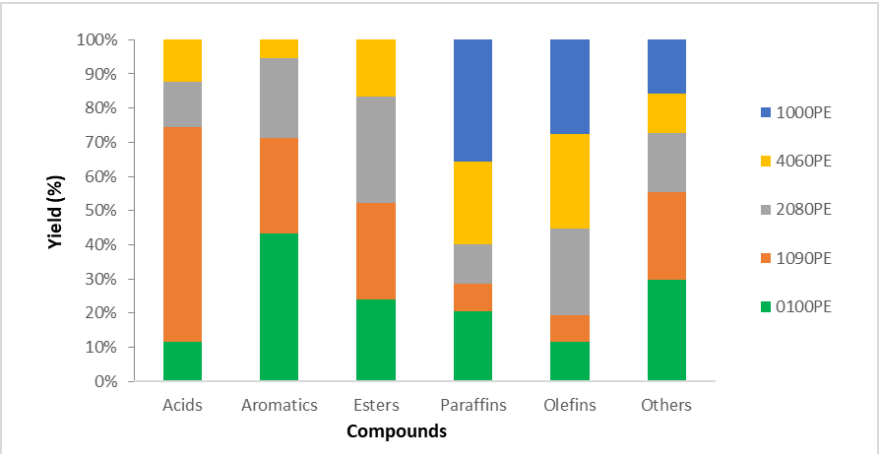
Figure 3: Effect of the Catalyst type and Catalyst Loading on the yield of Pyrolysis Products



4. Molecular Composition of the Oils from Co-Pyrolysis of EFB with LDPE

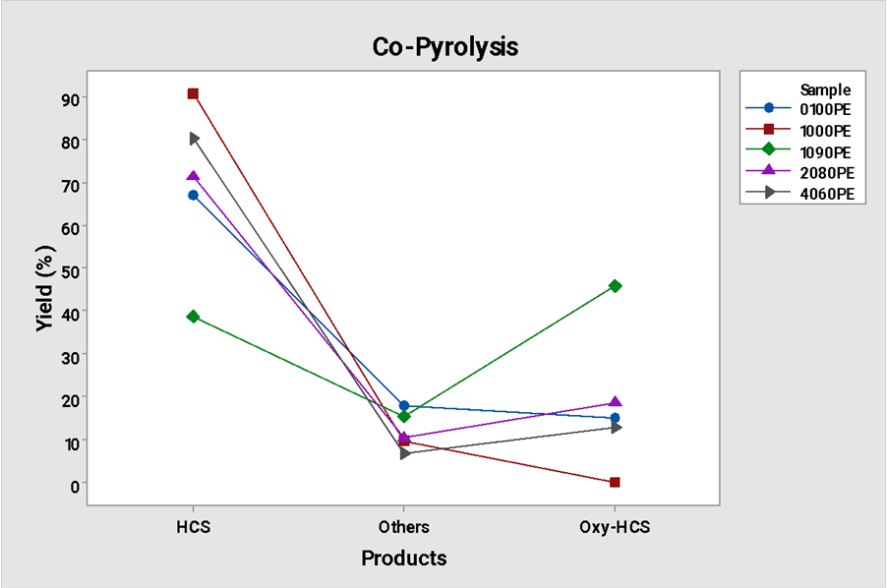
The oil derived from the co-pyrolysis seen in Figure 4 is an organic fraction together with its molecular makeup. The LDPE and EFB fibres worked in concert during the pyrolysis, according to the data. The oil from the 1090PE sample contained roughly 36% acidic chemicals, according to the GC-MS data. While olefins make up 50.21% of the oil obtained from the pyrolysis of a 4060PE sample. The oil obtained from the pyrolysis of a 1000PE sample is also composed of olefins (40.13%) and paraffins (50.14%). The synergistic impact exhibited by the radical interactions between biomass and polymers during the process is the reason why the relative fraction of aromatic compounds from the co-pyrolysis was seen to decrease with a decrease in the LDPE loading (Salema et al., 2019). Thus, Figure 5 displays a summary of the percentage composition of oxygenates and hydrocarbons.

Figure 4: Molecular Composition of Oils from thermal Co-pyrolysis



A significant increase in pyrolysis oil yield and improvement of the pyrolysis oil quality pointed out synergistic effects during the process. These effects may be positive or negative depending on several variables, including the type and contact of the component blending feedstock materials, duration of the pyrolysis, temperature and heating rate, removal or equilibrium of formed volatiles, and addition of solvents, catalysts, and hydrogen donors (Vuthaluru, 2004b). Therefore, it shows that slow and fast biomass pyrolysis processes are similar to co-pyrolysis and its blend using hydrogen-rich co-feeding elements such as waste plastics.

Figure 5: Molecular Composition of Oils from thermal Co-pyrolysis

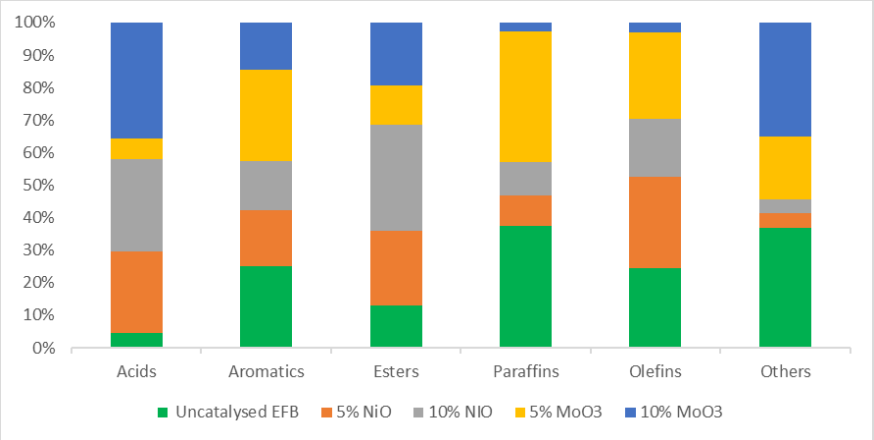


Key: HCS = Hydrocarbons, Oxy-HCS = Oxygenated Hydrocarbons

5. Molecular Composition of the Oils from Catalytic Pyrolysis of EFB Fiber

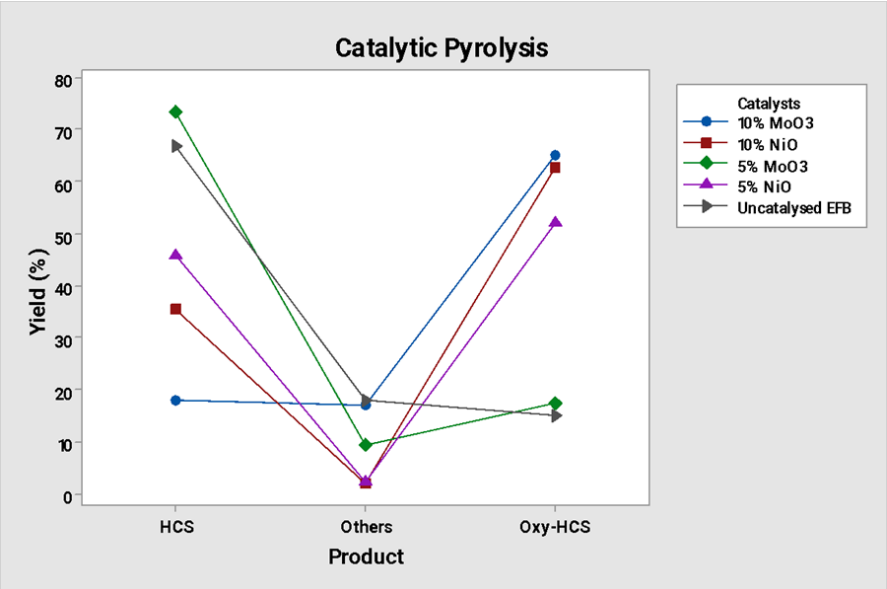
In Figure 6, the pyrolysis oil's molecular makeup is displayed. It becomes clear that the catalysts are highly selective to acidic compounds; the 10%MoO3 catalyst was most selective to acidic compounds, while it was less selective to paraffin and olefins. The amounts of aromatics, olefins, and paraffinic were almost equal in the 5%MoO3. The outcomes correspond with Wang et al.(Wang, 2020b) catalytic pyrolysis of woody biomass, which produced naphthalene and mild aromatics using CoMo-S catalyst.

Figure 6: Molecular Composition of Oils from Catalytic Pyrolysis



The largest percentage of hydrocarbons was produced with 5%MoO3, as Figure 7 illustrates. Conversely, the largest concentration of oxygenated molecules was achieved with 10% NiO, surpassing even the results of thermal pyrolysis. This may be explained by the catalysts' high acidic compound selectivity towards NiO.(Hamaguchi et al., 2012; Shafaghat, 2019)

Figure 7: Co-pyrolysis Gaseous Product Analysis



6. Gaseous Products Analyses from In-situ and Co-pyrolysis

The highest percentage of methane (CH4) from catalytic pyrolysis (5% MoO3; 39.70%) was likely the result of secondary cracking reactions, whereas the highest percentage from co-pyrolysis (4060PE; 38.10%) was likely the result of other processes. The non-condensable gaseous products from the thermal, catalytic, and co-pyrolysis processes are displayed in Figures 8 and 9 together with their percentage compositions can be related to the char's eventual breakdown, which the catalysts helped to facilitate.

Figure 8: Co-pyrolysis Gaseous Product Analysis

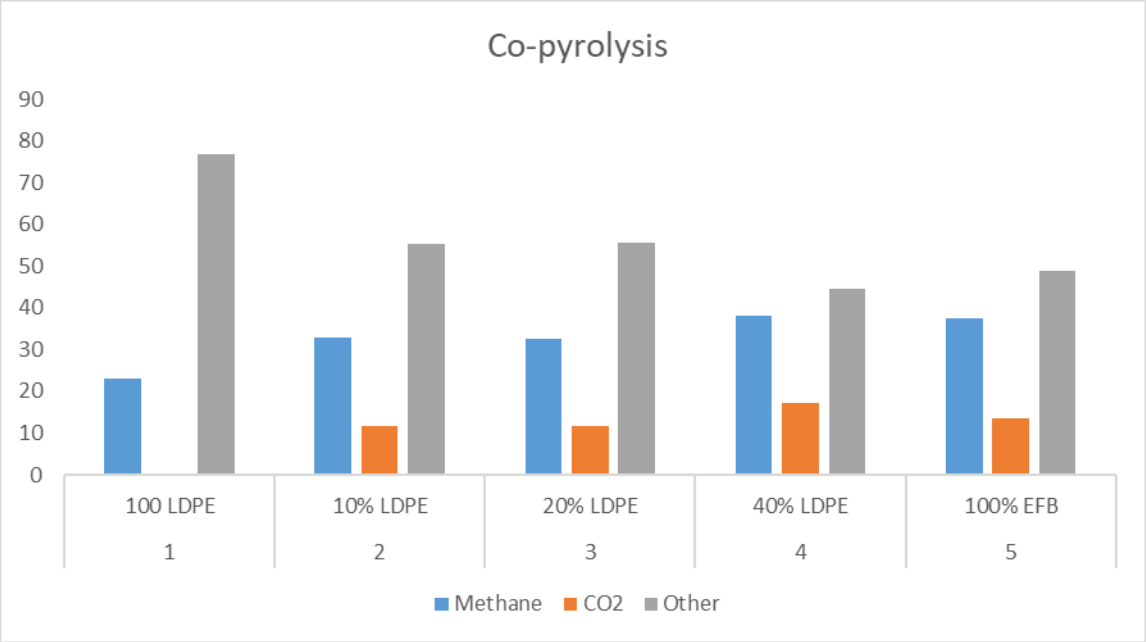
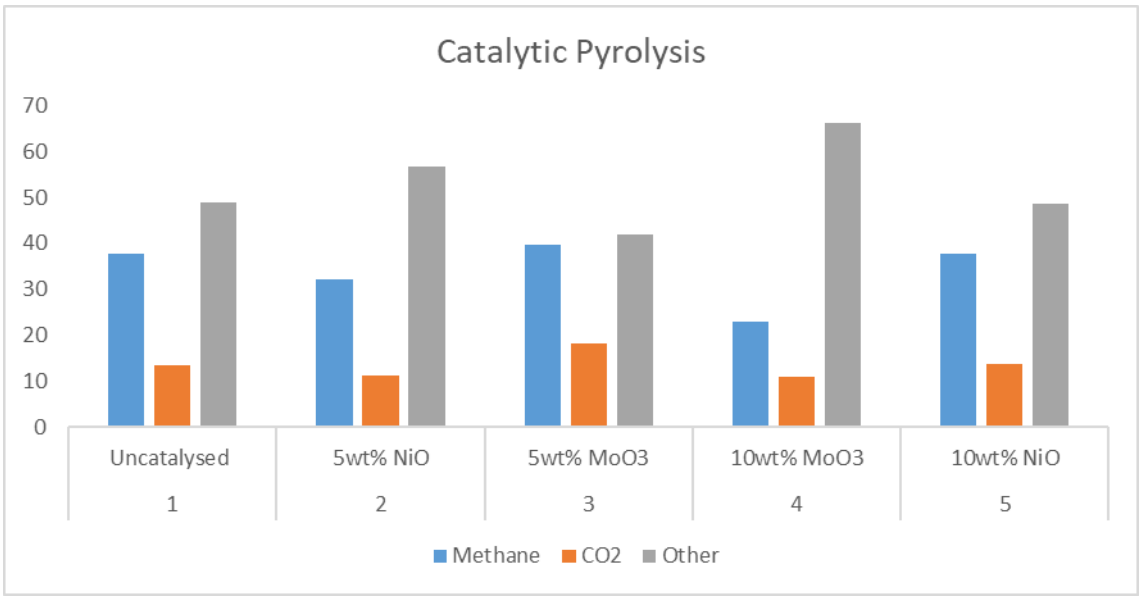


Figure 9: Catalytic pyrolysis Gaseous Product Analysis



This can be related to the char's eventual breakdown, which the catalysts helped to facilitate. The CO2 emission is mostly caused by the degradation of cellulose and hemicellulose. However, the release of CO2 at higher temperatures may potentially play a role in lignin breakdown (Lopez-Velazquez et al., 2013). Because of C-O breaking and subsequent hydrogen transfer, lignin's release of methoxy groups may also be related to CH4 gas and other light hydrocarbons.

CONCLUSION

The effect of temperature on the yield of pyrolysis products from EFB was examined, and the results suggested that 500°C was the optimal pyrolysis temperature. The effect of catalysts (NiO and MoO3) on the compositions of bio-oil from fiber pyrolysis indicated that the molecular composition of the pyrolysis oils formed hydrocarbons such as paraffins, olefins, and naphthenes during catalytic and co-pyrolysis.

The molecular composition of pyrolysis oils of EFB fibre and LDPE showed a synergistic effect on the product distribution of the liquid products. Highest percentage of pyrolysis oil yield was achieved at 500°C. The catalytic in-situ pyrolysis studied using MoO3 and NiO shows the selectivity of the acids on both the catalysts, which reduced with increased loading. The gaseous products collected from both In-situ and co-pyrolysis were hydrocarbon-rich gasses which could be sustainable and dependable sources of efficient energy.

Acknowledgement

We are grateful to Tertiary Education Trust Fund (TETFUND) for a PhD sponsorship through AST&D 2018 intervention.

Conflicts of Interest

We are confidence that there is of no any conflicts of interest associated with this publication, and there has been no financial support for this work that could have influenced its outcome. As Corresponding Author, I confirm that the manuscript has been read and approved for submission by all the named authors.

REFERENCE

Ayodele, O. B., Togunwa, O. S., Abbas, H. F., & Daud, W. M. A. W. (2014). Preparation and characterization of alumina supported nickel-oxalate catalyst for the hydrodeoxygenation of oleic acid into normal and iso-octadecane biofuel. *Energy Convers. Manag*, *88*, 1104–1110. https://doi.org/10.1016/j.enconman.2014.05.099.

Bajus, M. (2010). Pyrolysis technologies for biomass and waste treatment to fuels and chemical production. *Pet. Coal*, *52*(1), 1–10. www.vurup.sk/pc.

Barrett, J. A. (2016). Enhancing Aromatic Production from Reductive Lignin Disassembly: in Situ O-Methylation of Phenolic Intermediates. *ACS Sustain. Chem. Eng*, *4*(12), 6877–6886. https://doi.org/10.1021/acssuschemeng.6b01827.

Chong, Y. Y., Thangalazhy-Gopakumar, S., Ng, H. K., Lee, L. Y., & Gan, S. (2019). Effect of oxide catalysts on the properties of bio-oil from in-situ catalytic pyrolysis of palm empty fruit bunch fiber. *J. Environ. Manage*, *247*, 38–45. https://doi.org/10.1016/J.JENVMAN.2019.06.049.

Collin, S. M. A., Wan, G. J., Ashri, M., & Wan, B. (2015). *Preparation and characterization of activated carbon from Typha orientalis leaves* (pp. 9–21). https://doi.org/10.1007/s40090-014-0027-3.

Demirbas, A. (2009). Biorefineries: Current activities and future developments. *Energy Convers. Manag*, *50*(11), 2782–2801. https://doi.org/10.1016/j.enconman.2009.06.035.

Dickerson, T., & Soria, J. (2013). Catalytic fast pyrolysis: A review. *Energies*, *6*(1), 514–538. https://doi.org/10.3390/en6010514.

Dutta, S., & Pal, S. (2014). Promises in direct conversion of cellulose and lignocellulosic biomass to chemicals and fuels: Combined solvent-nanocatalysis approach for biorefinary. *Biomass and Bioenergy*, *62*, 182–197. https://doi.org/10.1016/j.biombioe.2013.12.019.

Hadi, B., Sokoto, A. M., Garba, M. M., & Muhammad, A. B. (2017). Effect of neat kaolin and CuO/Kaolin on the yield and composition of products from pyrolysis of polystyrene waste. *Energy Sources, Part A Recover. Util. Environ. Eff*, *39*(2), 148–153. https://doi.org/10.1080/15567036.2016.1201548.

Hamaguchi, M., Cardoso, M., & Vakkilainen, E. (2012). Alternative technologies for biofuels production in kraft pulp mills-potential and prospects. *Energies*, *5*(7), 2288–2309. https://doi.org/10.3390/en5072288.

Hazrat, M. A., Rasul, M. G., Khan, M. M. K., Azad, A. K., & Bhuiya, M. M. K. (2014). Utilization of polymer wastes as transport fuel resources- a recent development. *Energy Procedia*, *61*, 1681–1685. https://doi.org/10.1016/j.egypro.2014.12.191.

Idris, R. (2021). Phenol-rich bio-oil derivation via microwave-induced fast pyrolysis of oil palm empty fruit bunch with activated carbon. *Environ. Technol. Innov*, *21*, 101291. https://doi.org/10.1016/J.ETI.2020.101291.

Idris, R., Chong, C. T., Asik, J. A., & Ani, F. N. (2020). Optimization studies of microwave-induced co-pyrolysis of empty fruit bunches/waste truck tire using response surface methodology. *J. Clean. Prod*, *244*, 118649. https://doi.org/10.1016/J.JCLEPRO.2019.118649.

Kilby, P. (1967). *The Nigerian palm oil industry* (Vol. 1965, pp. 1945–1965).

Kimia, P., Tandan, B., Buah, K., & Sawit, K. (2017). *Chemical and Physical Characterization of Oil Palm Empty* (Vol. 21, Issue 1, pp. 188–196).

Krutof, A. (2018). *Upgrading of biomass sourced pyrolysis oil review : focus on co-pyrolysis and vapour upgrading during pyrolysis*.

Kumar, P., Yenumala, S. R., Maity, S. K., & Shee, D. (2014). Kinetics of hydrodeoxygenation of stearic acid using supported nickel catalysts: Effects of supports. *Appl. Catal. A Gen*, *471*, 28–38. https://doi.org/10.1016/j.apcata.2013.11.021.

L. Barrientos, S. R.-L. J. M. P. J. N. Y. and V. L. (2009). *UNVEILING THE STRUCTURE OF NI/NI OXIDE NANOPARTICLES SYSTEM*.

Lindfors, C. (2009). Production of bio-oil from forest residue. *Nord. Wood Biorefinery Conf*, *2*(1).

Lindfors, C. (2019). In-situ and ex-situ catalytic pyrolysis/co-pyrolysis of empty fruit bunches using mesostructured aluminosilicate catalysts. *Chem. Eng. J*, *366*(February), 330–338. https://doi.org/10.1016/j.cej.2019.02.055.

Lødeng, R. (2017). Hydrodeoxygenation of phenolics in liquid phase over supported MoO3 and carburized analogues. *Biomass Convers. Biorefinery*, *7*(3), 343–359. https://doi.org/10.1007/s13399-017-0252-z.

López-González, D., Fernandez-Lopez, M., Valverde, J. L., & Sanchez-Silva, L. (2013). Thermogravimetric-mass spectrometric analysis on combustion of lignocellulosic biomass. *Bioresour. Technol*, *143*, 562–574. https://doi.org/10.1016/j.biortech.2013.06.052.

Lopez-Velazquez, M. A., Santes, V., Balmaseda, J., & Torres-Garcia, E. (2013). Pyrolysis of orange waste: A thermo-kinetic study. *Journal of Analytical and Applied Pyrolysis*, *99*, 170–177. https://doi.org/10.1016/j.jaap.2012.09.016

Mlynková, B., Hájeková, E., & Bajus, M. (2008). Copyrolysis of oils/waxes of individual and mixed polyalkenes cracking products with petroleum fraction. *Fuel Process. Technol*, *89*(11), 1047–1055. https://doi.org/10.1016/j.fuproc.2008.04.007.

Muhammad, F., U., M., Hadi, B. A., Muhammed, S., & Usman. (2021). Thermal and Catalytic Conversion of Native Rice Husk into Bio-Oil and Biochar. *Int. J. Sci. Glob. Sustain*, *7*(1), 1–8. https://doi.org/doi:

Mukarakate, C. (2014). Upgrading biomass pyrolysis vapors over β-zeolites: Role of silica-to-alumina ratio. *Green Chem*, *16*(12), 4891–4905. https://doi.org/10.1039/c4gc01425a.

Otti, V. I., Ifeanyichukwu, H. I., Nwaorum, F. C., & Ogbuagu, F. U. (2014). Sustainable Oil Palm Waste Management in Engineering Development. *Civ. Environ. Res*, *6*(5), 121–126.

Panda, A. K., & Singh, R. K. (2011). Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene. *J. Fuel Chem. Technol*, *39*(3), 198–202. https://doi.org/10.1016/S1872-5813(11)60017-0.

Patel, J. M., Patel, K. J., Patel, V. V, & Vaghela, K. V. (2013). *Performance studies of Tire Pyrolysis Oil blends with Diesel Fuel* (Issue 2, pp. 219–221).

Salema, A. A., Ting, R. M. W., & Shang, Y. K. (2019). Pyrolysis of blend (oil palm biomass and sawdust) biomass using TG-MS". *Bioresource Technology*, *274*, 439–446. https://doi.org/10.1016/j.biortech.2018.12.014

Salman, B., Nomanbhay, S., & Salema, A. A. (2019). Microwave-synthesised hydrothermal co-pyrolysis of oil palm empty fruit bunch with plastic wastes from Nigeria. *Biofuels*, *0*(0), 1–17. https://doi.org/10.1080/17597269.2019.1626000.

Shafaghat, H. (2019). In-situ and ex-situ catalytic pyrolysis/co-pyrolysis of empty fruit bunches using mesostructured aluminosilicate catalysts. *Chem. Eng. J*, *366*(February), 330–338. https://doi.org/10.1016/j.cej.2019.02.055.

Sharma, A. K., Desnavi, S., Dixit, C., Varshney, U., & Sharma, A. (2015). *Extraction of Nickel Nanoparticles from Electroplating Waste their application in production of Bio-Diesel from Biowaste*. https://doi.org/10.7763/IJCEA.2015.V6.472.

Sukiran, M. A., Bakar, N. K. A., & Chin, C. M. (2009). Optimization of pyrolysis of oil palm empty fruit bunches. *J. Oil Palm Res*, *21*(DECEMBER), 653–658.

Sukiran, M. A., Kheang, L. S., Bakar, N. A., & May, C. Y. (2014). Pyrolysis of empty fruit bunches: Influence of temperature on the yields and composition of gaseous product. *Am. J. Appl. Sci*, *11*(4), 606–610. https://doi.org/10.3844/ajassp.2014.606.610.

Vuthaluru, H. B. (2004a). Investigations into the pyrolytic behaviour of coal/biomass blends using thermogravimetric analysis. *Bioresour. Technol*, *92*(2), 187–195. https://doi.org/10.1016/j.biortech.2003.08.008.

Vuthaluru, H. B. (2004b). Investigations into the pyrolytic behaviour of coal/biomass blends using thermogravimetric analysis. *Bioresource Technology*, *92*(2), 187–195. https://doi.org/10.1016/j.biortech.2003.08.008

Wang, L. (2020a). *Morphology evolution and quantitative analysis of β - MoO 3 and a - MoO 3* (pp. 620–626).

Wang, L. (2020b). Morphology evolution and quantitative analysis of β-MoO3 and α- MoO3. *High Temperature Materials and Processes*, *39*(1), 620–626.

Won, J. (2016). Highly microporous carbon materials synthesized from fl uorine-containing poly (amic acid) adsorbed in polystyrene cryogel template. *Synth. Met*, *211*, 35–39. https://doi.org/10.1016/j.synthmet.2015.11.009.

Wong, S. L., Ngadi, N., Abdullah, T. A. T., & Inuwa, I. M. (2015). Current state and future prospects of plastic waste as source of fuel : A review. *Renew. Sustain. Energy Rev*, *50*, 1167–1180. https://doi.org/10.1016/j.rser.2015.04.063.

Xue, Y., Zhou, S., Brown, R. C., Kelkar, A., & Bai, X. (2015). Fast pyrolysis of biomass and waste plastic in a fluidized bed reactor. *Fuel*, *156*, 40–46. https://doi.org/10.1016/j.fuel.2015.04.033.

Yoo, H. M., Park, S. W., Seo, Y. C., & Kim, K. H. (2019). Applicability assessment of empty fruit bunches from palm oil mills for use as bio-solid refuse fuels. *J. Environ. Manage*, *234*, 1–7. https://doi.org/10.1016/j.jenvman.2018.11.035.

Zhang, B., Zhong, Z., Ding, K., & Song, Z. (2015). Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high density polyethylene: Analytical Py-GC/MS study. *Fuel*, *139*, 622–628. https://doi.org/10.1016/j.fuel.2014.09.052.

Zhang, J., Chen, S., Yang, R., & Yan, Y. (2010). Biodiesel production from vegetable oil using heterogenous acid and alkali catalyst. *Fuel*, *89*(10), 2939–2944. https://doi.org/10.1016/j.fuel.2010.05.009.