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THE EFFECT OF TEMPERATURE ON CO-PYROLYSIS OF EMPTY FRUIT BUNCH AND USED PALM COOKING OIL FOR HYDROCARBON FUEL PRODUCTION

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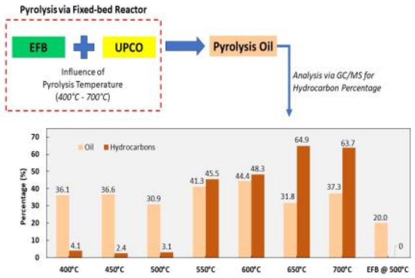
Graphical abstract



Abstract

This research is significant in renewable energy and waste management, focusing on the co-pyrolysis of empty fruit bunch (EFB) and used palm cooking oil (UPCO) to convert biomass waste into valuable hydrocarbon fuels. Thus, the main goal of this research is to investigate the influence of temperature on the co-pyrolysis of empty fruit bunch (EFB) and used palm cooking oil (UPCO) into hydrocarbon fuel via a fixed-bed reactor. The EFB to UPCO mass ratio was fixed at 1:1, and the temperature varied from 400 to 700°C at 50°C intervals. The generated pyrolysis oil at each temperature was analysed via Gas Chromatography/Mass Spectrometer for organic compositions. Pyrolysis of EFB also was investigated at 500°C for comparison purposes. The results show that adding UPCO increased the pyrolysis yield at all investigated temperatures compared to pyrolysis of EFB only, with the highest pyrolysis oil yield achieved at 600°C (44.4%). The hydrocarbon yield was also significantly influenced by UPCO with varying temperature conditions. The highest hydrocarbon yield of 64.9% was achieved at 650°C followed in descending order as follows: 700°C (63.7%) > 600 °C (48.3%), 550 °C (45.5%), 400°C (4.1%), 500°C (3.1%), 450°C (2.4%) and EFB at 500°C (0%). In pyrolysis oil, oxygenated compounds such as phenols, ketones, aldehydes, acids, furans, esters, and ethers decreased significantly by 45.5 to 64.9% from 550 °C to 700 °C. In conclusion, this study supports the transition towards cleaner energy alternatives, aligning with global sustainability goals and the growing demand for environmentally friendly fuel sources.

Keywords: Biomass, cooking oil, pyrolysis, hydrocarbons, fuel

Abstrak

Penyelidikan ini mempunyai kepentingan besar dalam konteks tenaga boleh diperbaharui dan pengurusan sisa. Dengan menyelidiki ko-pirolisis tandan kosong kelapa sawit (EFB) dan minyak masak kelapa sawit terpakai (UPCO), kajian ini bertujuan untuk menukar sisa biojisim kepada bahan api hidrokarbon yang bernilai, sekali gus menangani isu alam sekitar yang berkaitan dengan pembuangan sisa. Oleh itu, matlamat utama penyelidikan ini adalah untuk menyelidiki pengaruh suhu terhadap ko-pirolisis EFB dan UPCO kepada bahan api hidrokarbon melalui reaktor. Nisbah jisim EFB kepada UPCO ditetapkan pada 1:1, dan suhu diubah dari 400 hingga 700°C pada selang 50°C. Minyak pirolisis yang dihasilkan pada setiap suhu dianalisis menggunakan Gas Chromatography/Mass Spectrometer untuk komposisi organik. Pirolisis EFB juga dikaji pada suhu 500°C untuk tujuan perbandingan. Hasil kajian menunjukkan bahawa penambahan UPCO meningkatkan hasil pirolisis pada semua suhu yang diselidiki berbanding pirolisis EFB sahaja, dengan hasil minyak pirolisis tertinggi dicapai pada suhu 600°C (44.4%). Hasil hidrokarbon juga dipengaruhi secara signifikan oleh UPCO dengan variasi suhu yang berbeza. Hasil hidrokarbon tertinggi sebanyak 64.9% dicapai pada suhu 650°C diikuti dalam urutan menurun seperti berikut: 700°C (63.7%) > 600°C (48.3%), 550°C (45.5%), 400°C (4.1%), 500°C (3.1%), 450°C (2.4%) dan EFB pada suhu 500°C (0%). Dalam minyak pirolisis, sebatian beroksigen seperti fenol, keton, aldehid, asid, furan, ester, dan eter menurun dengan ketara sebanyak 45.5 hingga 64.9% dari 550°C hingga 700°C. Kesimpulannya, kajian ini menyokong peralihan ke arah alternatif tenaga yang lebih bersih, sejajar dengan matlamat kelestarian global dan permintaan yang semakin meningkat untuk sumber bahan api mesra alam.

1.0 INTRODUCTION

The demand for additional material and energy consumption rises along with population growth. As a result, there has been a constant rise in the need for energy. The primary energy source used today is petroleum and demand for it is anticipated to rise [1]. Petroleum-based products power vehicles, heat buildings, and generate energy. Similarly, Malaysia's energy industry is primarily reliant on conventional fossil fuel resources, with 88.4% constituting fossil fuels, which can be further broken down to account for 53.3% natural gas, 30.5% coal, 2.8% fuel oil, and 1.8% diesel with hydropower accounting for the remainder [2]. However, switching to sustainable renewable energy is advised to satisfy the projected increase in energy demand due to the depletion of fossil fuel reserves and their detrimental effects on the environment.

One of the most significant renewable energy sources that can meet the demands of the expanding industry is biomass. Biomass is a renewable energy source and contains hydrogen and carbon compositions, which have gained the attention of researchers. In addition, biomass is sustainable and low-cost as we are now realising the importance of finding alternatives to non-renewable energy such as fossil fuels. Interestingly, Malaysia's biomass availability is predicted to be roughly 47,402 dry kilotons per year [3]. A typical oil palm mill produces solid waste in the form of squeezed fibre, empty fruit bunches (EFB), and kernel shells from 70% of the inflow (fresh fruit bunches). Pyrolysis is the most promising technology in utilizing biomass into biofuel (also known as pyrolysis oil) that can potentially replace conventional fuel in the future [4]. This is because biomass-derived biofuel (BDB) exhibits the advantages of easy handling, low nitrogen and sulphur contents, which it produces fewer nitrogen oxides (NOx) and sulphur oxides (SOx) when combusted compared to the combustion of fossil fuels [5]. However, BDB also exhibits drawbacks such as high oxygen content (35-40%) which prohibits it from being used as immediate conventional fuel [6]. This is because high oxygen-containing compounds reduce the energy content and thermal stability of BDB. Additional undesirable properties of BDB that make it not fit to use include high water content and viscosity [7]. Therefore, BDB properties need to be upgraded by converting oxygenates into hydrocarbons to replace fossil fuels. Synergistic interactions between produced intermediates can improve the output and quality of BDB by co-pyrolyzing biomass with hydrogen and carbon-rich materials [8].

Recently, co-pyrolysis has been widely investigated and is recommended for upgrading BDB properties [9]. This is because co-pyrolysis tends to create synergy between various feedstock which can efficiently upgrade BDB properties. Co-pyrolysis is defined as the pyrolysis of more than one type of feedstock. Co-pyrolysis could induce dehydrogenation by actively cracking heavy compounds into hydrocarbons and eventually increasing the high heating value (HHV) of biofuel [10]. Many studies have used hydrogen gas (H_2) as a medium in biomass pyrolysis for dehydrogenation, but H_2 is categorized as an expensive medium [11]. Hence, a promising and inexpensive feedstock is required in co-pyrolysis with biomass. Currently, plastic waste (PW), waste tyre (WT), and coal have been extensively used as feedstock mixed with biomass or biomass model compounds in co-pyrolysis [11].

On the other hand, palm-based cooking oil is bio-based oil used for frying, cooking, and other sorts of processing in homes, fast food establishments, restaurants, and the food production sector [12]. Dada *et al.* (2022) [13] reported that cooking oil will undergo physical and chemical changes due to chemical reactions such as hydrolysis, heat deterioration, oxidation, and polymerization during these processes. They also added that cooking oil includes a lot of free fatty acids, which emit a strong odour and cause concrete and metal components to corrode. Furthermore, because it has the potential to harm the environment seriously, this dumping has been labelled as a type of municipal garbage which includes domestic waste as well as comparable commercial, industrial, and institutional wastes. However, cooking oil still exhibits bio-resource properties that are underutilised in urban settings and have potential in the sectors of energy and materials [14]. Recycling cooking oil offers a sustainable source of feedstock for making bio-based goods, but it also reduces greenhouse gas (GHG) emissions and prevents environmental degradation brought on by inappropriate handling, such as landfilling. In a study by Azman *et al.* (2021) [15], used cooking oil showed high hydrocarbon fraction yields of 89.93% due to chemical compounds released during the high cooking temperatures at ideal circumstances within C_{14}–C_{18} hydrocarbons. Hence, with the chemical properties of used cooking oil, the addition of it as co-feedstock in the pyrolysis of EFB could improve the yield and convert most oxygenated compounds into hydrocarbons.

To the best of our knowledge, studies on the co-pyrolysis of EFB and used palm cooking oil (UPCO) into pyrolysis oil rich in hydrocarbons are still lacking in the literature. Thus, this study investigated the influence of UPCO on the pyrolysis of EFB into pyrolysis oil rich in hydrocarbons at varied temperatures (400–700°C). This research is significant for improving biofuel generation during pyrolysis and for minimising biomass and used palm cooking oil.

2.0 METHODOLOGY

2.1 Empty Fruit Bunch Preparation

Empty fruit bunch (EFB) was purchased from a local palm mill company in Selangor, Malaysia. The preparation of EFB was reported in our previous work [16].

2.2 Used Palm Cooking Oil Preparation

Used palm cooking oil (UPCO) was collected from nearby restaurants in the Kuala Lumpur area. The UPCO was cooled down to room temperature before being filtered to remove any food debris that was left in the UPCO. Next, the filtered UPCO was heated to 110°C to remove any moisture content. Finally, the UPCO was stored in a tight container to avoid any moisture absorption.

2.3 Pyrolysis via Fixed-Bed Reactor

The effect of temperature in co-pyrolysis of EFB and UPCO was investigated via a fixed-bed reactor as illustrated in Figure 1. The EFB to UPCO mass ratio was fixed at 1:1 and the pressure was maintained at 1 atm. Pyrolysis experiments were performed in batch runs at varying temperatures from 400 to 700°C at an interval of 50°C. Nitrogen (N_2) gas was purged at a constant flow rate of 50 mL/min from the inlet to the outlet of the reactor to create an inert atmosphere and also to flow vapours from the reactor into the condenser during pyrolysis. In addition, pyrolysis of EFB is also conducted at 500°C for benchmarking purposes.

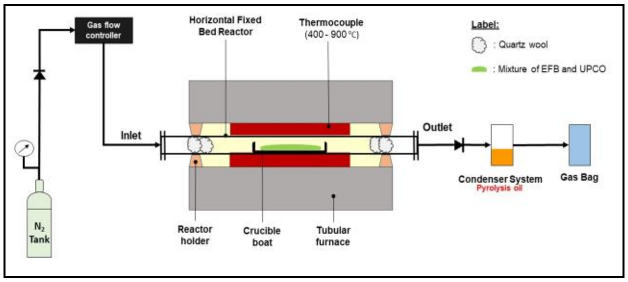


Figure 1 Schematic diagram of pyrolysis system

Condensed pyrolysis oil was collected for organic composition analysis via gas chromatography-mass spectrometer (GC/MS). The standard operating procedures of GC/MS for pyrolysis oil were reported in our previous work [17]. Non-condensable vapours were collected via a gas bag. Finally, after each experiment, the reactor was shut off and allowed to cool down slowly to collect char. All the product yields were calculated based on our previous work [17]. All the experiments were conducted two times to lower the errors.

3.0 RESULTS AND DISCUSSION

3.1 Pyrolysis Product Yield

Figure 2 illustrates the pyrolysis product distributions from co-pyrolysis of EFB and UPCO at temperatures ranging from 400 to 700°C. Among the tested pyrolysis samples, the highest pyrolysis oil yield of 44.4

wt.% was achieved at 600 °C, followed by 550°C (41.3 wt.%) > 700°C (37.3 wt.%) > 450°C (36.6 wt.%) > 400°C (36.1 wt.%) > 650°C (31.8 wt.%) > 500°C (30.9 wt.%).

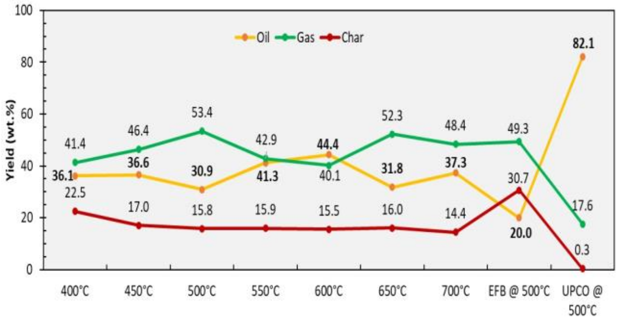


Figure 2 Pyrolysis product yield (%)

As shown in Figure 2, it was observed that the pyrolysis oil yield fluctuates with increasing temperature from 400 to 700°C. In detail, an increment in pyrolysis oil was observed from 500 to 600°C, this could be due to the increment in heat energy which easily breaks down the EFB and UPCO into condensable oil. Similarly, Liu *et al.* (2017) [18] stated that an increase in temperatures would gradually increase the devolatilization rate, leading to strong organic bonds being broken. This is one potential explanation for the rising pyrolysis oil yield. However, after 600°C a decrease in pyrolysis oil yield was observed which could be due to the increment in heat energy which further enhanced the cracking process also known as secondary cracking of EFB and UPCO and eventually produced lighter compounds in the form of non-condensable gases.

Notably, as can be seen in Figure 2, higher gas yield than oil yield was achieved at temperatures below 600°C. This situation could be contributed by UPCO which has a boiling point of 300°C as reported by Yaakob *et al.* (2013) [19]. In other words, at 400°C the UPCO starts to break down into non-condensable volatiles that have contributed to higher gas yield than oil yield. Meanwhile, for the char yield, it was found that an almost consistent yield was achieved from 450 to 700°C ranging from 14.4–17.0 wt.%, except at 400°C which has achieved the highest char yield of 22.5 wt.%. This might be due to the low temperature of 400°C which has insufficient heat energy to break down EFB structure and chemical bonds in UPCO into volatile products.

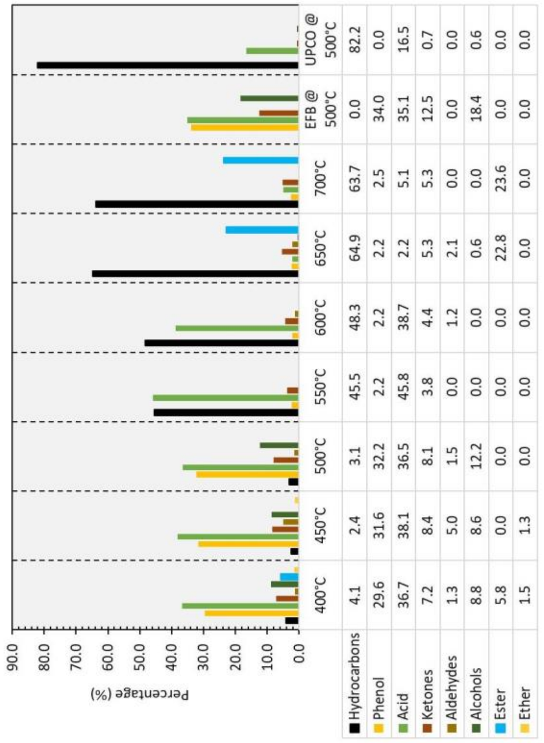
All the co-pyrolysis of EFB and UPCO samples was compared with pyrolysis of EFB in terms of product yields as shown in Figure 2. It can be concluded that the addition of UPCO into the pyrolysis of EFB has significantly enhanced the oil yield by lowering the char yield. Other than that, the higher pyrolysis oil yield for all the EFB and UPCO samples could also be due to the properties of UPCO which can easily break down into volatiles at temperatures of 400 to 700°C compared to pyrolysis of EFB. In detail, UPCO breaks into volatiles earlier than EFB due to the low thermal degradation point which these UPCO volatiles will eventually act as cracking enhancers in breaking down the energy barrier in the EFB structure with the support of heat energy. This shows that UPCO increases the yield of desired products and increases the effectiveness of the pyrolysis process. However, in the pyrolysis process, the oil content of UPCO is crucial. A significant portion of UPCO is made up of fats and oils, which are high in energy and can help co-pyrolysis yield more valuable products. These fats and oils function as an additional source of hydrogen and carbon, increasing the overall carbon yield and encouraging the creation of favourable pyrolysis products.

3.2 Organic Compositions in Pyrolysis Oil

Hydrocarbons, phenols, acids, ketones, aldehydes, alcohols, furan, esters and ethers can be categorised as relative components of pyrolysis oil from co-pyrolysis of EFB and UPCO as shown in Figure 3. The objective of this work is to elucidate the synergetic effect of temperature (400 to 700°C) with the application of UPCO in the pyrolysis of EFB in producing hydrocarbons with low oxygenated compounds in pyrolysis oil. In general, biomass is made of complex lignocellulosic structures such as hemicellulose, cellulose, and lignin that can be converted into pyrolysis oil via pyrolysis. Thus, the pyrolysis of biomass generally produces oxygenated pyrolysis oil with little or no hydrocarbons. Similarly, in this study, the pyrolysis oil from the pyrolysis of EFB at 500°C was analysed via GC/MS and it was found that six types of oxygenated compounds such as phenols (34.0%), acids (35.1%), ketones (12.5%), and alcohols (18.4%) with 0% of hydrocarbons were present in pyrolysis oil as depicted in Figure 3. The high-oxygenated compounds in pyrolysis oil have many drawbacks such as high viscosity and high acidity which limits its direct applications [20]. Thus, it is important to upgrade oxygenated pyrolysis oil into hydrocarbon fuel for a beneficial profit.

On the other hand, the thermal degradation profile of Used Palm Cooking Oil (UPCO) at 500°C reveals a distinctive composition with a high concentration of hydrocarbons, which constitute 82.2% of the total yield, as illustrated in Figure 3. This significant yield of hydrocarbons at this temperature indicates effective cracking of the oil's triglycerides into smaller, energy-rich hydrocarbon chains, making it a promising option for biofuel production. Interestingly, the absence of phenolic compounds in UPCO at 500°C sets it apart from other samples, such as Empty Fruit Bunch (EFB), at the same temperature. Phenolic compounds are usually produced from lignin degradation, which is not present in UPCO due to its lipid-based composition. This lack of phenols may be beneficial for applications that require low-oxygenated compounds, as phenolic substances can increase the oxygen content in the product, ultimately reducing its fuel quality.

Acids are present at a lower percentage (16.5%) than hydrocarbons. This moderate level of acid formation may be linked to the breakdown of fatty acids in the oil. However, it is significantly lower than what would typically be expected in raw, untreated oils. This suggests that at a temperature of 500°C, some decarboxylation reactions occur, leading to a reduction in acid content and an increase in hydrocarbon production. Minor compounds include ketones (0.7%) and alcohols (0.6%), while aldehydes and ethers are absent. The low presence of oxygenated compounds such as ketones and alcohols indicate the relative stability of these structures during the UPCO pyrolysis process. Additionally, the absence of esters suggests a complete breakdown or transformation of these groups, further reinforcing the preference for hydrocarbon formation under these conditions. Overall, this outcome positions UPCO as a promising feedstock for biofuel production at moderate pyrolysis temperatures, potentially enhancing hydrocarbon yields.



	400°C	450°C	500°C	550°C	600°C	650°C	700°C	EFB @ 500°C	UPCO @ 500°C
■ Hydrocarbons	4.1	2.4	3.1	45.5	48.3	64.9	63.7	0.0	82.2
■ Phenol	29.6	31.6	32.2	2.2	2.2	2.2	2.5	34.0	0.0
■ Acid	36.7	38.1	36.5	45.8	38.7	2.2	5.1	35.1	16.5
■ Ketones	7.2	8.4	8.1	3.8	4.4	5.3	5.3	12.5	0.7
■ Aldehydes	1.3	5.0	1.5	0.0	1.2	2.1	0.0	0.0	0.0
■ Alcohols	8.8	8.6	12.2	0.0	0.0	0.6	0.0	18.4	0.6
■ Ester	5.8	0.0	0.0	0.0	0.0	22.8	23.6	0.0	0.0
■ Ether	1.5	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Figure 3 Organic compositions in pyrolysis oil

Interestingly, it was found that the addition of UPCO in the pyrolysis of EFB plays a significant role in promoting the production of hydrocarbons in pyrolysis oil at 400 to 700°C as shown in Figure 3. The highest hydrocarbon content in pyrolysis oil can be observed at 650°C (64.9%), followed by 700°C (63.7%) > 600°C (48.3%) > 550°C (45.5%) > 400°C (4.1%) > 500°C (3.1%) > 450°C (2.4%). The significant increase in hydrocarbon content of more than 45% in pyrolysis oil starts at 550 to 700°C and below 550°C is in the range of 2.4 to 4.1%. This might be due to the synergistic effect of temperature and UPCO in cracking the complex structure of EFB and boosting the hydrocarbon contents in pyrolysis oil. In detail, the pyrolysis of EFB breaks the chemical bonds in the lignocellulosic structure into oxygenated vapours and the fatty acids vapours from UPCO further break the oxygenated vapours into hydrocarbons by possibly eliminating the oxygen via decarboxylation, decarbonylation, and dehydration. Meanwhile, the hydrocarbon composition dipped a little to 63.7% at 700°C. This is highly possible due to secondary events such as additional cracking or disintegration of hydrocarbons into non-condensable light hydrocarbons at higher temperatures of more than 650°C. This is consistent with the result as shown in Figure 2 for co-pyrolysis of EFB and UPCO at 700°C which produces the lowest char yield at 14.4 wt.% which means more cracking has occurred at temperature above 650°C.

The production pattern of phenols in pyrolysis oil from 400 to 700°C is an inverse pattern of hydrocarbon production. For example, it was observed that the pyrolysis of EFB produces 35.8% of phenols which is almost a similar percentage of 35.0 – 39.5% at 400 to 500°C. Meanwhile, the percentage of phenols dropped drastically at 550 to 700°C with a significant increase in hydrocarbon percentage. Hence, it can be assumed that the fatty acid vapours from UPCO played a major role in breaking the hydroxyl group in phenol via deoxygenation into hydrocarbons. Generally, lignin in biomass is the major contributor to phenols production in pyrolysis oil which degrades at a temperature range between 150 to 900°C [21].

Based on Figure 3, it can be concluded that the pyrolysis oil from the pyrolysis of EFB at 500°C is highly acidic due to a high acid percentage of 17.3%. Consequently, the addition of UPCO in the pyrolysis of EFB has increased the acid content in a decreasing pattern from 400°C (36.7%) to 450°C (32.7%) to 500°C (24.2%). The higher acid contents at this temperature range could be due to the free fatty acid content in UPCO. On the other hand, it can be concluded that the acid contents in pyrolysis oil decrease with increasing temperature from 400 to 500°C. In detail, the higher temperature can break the free fatty acids from UPCO into lighter compounds which could act as hydrocarbon enhancers. This is consistent with acid contents observed at 550°C and above which drastically dropped in between 1.8–6.2%.

On the other hand, based on Figure 3, it was observed that the ester contents had significantly increased at 550°C and above in a decrease pattern from 550°C (46.3%) > 600°C (37.0%) > 650°C (23.3%) > 700°C (23.5%). Meanwhile, the pyrolysis of EFB produces esters at 9.0%. Generally, UPCO has a high potential to be converted into methyl ester during pyrolysis [22]. In detail, in this study, during the co-pyrolysis of EFB and UPCO, the higher temperatures (≥550°C) stimulated UPCO to have thermally cracked into ester without the presence of catalyst. Hence, it can be drawn that the pyrolysis of UPCO can produce a high percentage of esters (46.3%) with an almost equal percentage of hydrocarbons at 45.5%, but it requires a very high temperature (refer Figure 3).

For ketones in pyrolysis oil, it can be observed that the pyrolysis of EFB produces ketones at 6.9% as shown in Figure 3. Ketones are distinguished by a carbonyl group (C=O) linked to two carbon atoms. They are created by the molecular structure of the original biomass ingredients being broken up and reorganized. In contrast, a slight increase in ketones in the range of 7.2 to 8.4% can be observed in pyrolysis oil from co-pyrolysis of EFB and UPCO at 400 to 500°C. Thus, the addition of UPCO at 400 to 500°C in the pyrolysis of EFB did not greatly influence the conversion of ketones into other compounds. Meanwhile, lower ketone contents were observed at co-pyrolysis of EFB and UPCO at 550 to 700°C. Thus, a temperature above 500°C plays a crucial role in cracking ketones into other compounds, unlike UPCO.

Other than ketones, aldehydes can be found in pyrolysis oil at all temperatures except at 550°C and 700°C. Usino *et al.* (2021) [23] reported that the thermal degradation of the hemicellulose in biomass is a possible cause of the aldehydes production. In contrast, in this study, there was no production of aldehydes in pyrolysis oil from the pyrolysis of EFB at 500°C. Meanwhile, pyrolysis oil from all co-pyrolysis of EFB and UPCO samples produces a low percentage of aldehydes in the range of 1.2 to 5.0%. Another contributing factor could be triglycerides, the primary constituents of UPCO that degrade thermally. Comparable research was found by Peng *et al.* (2017) [24] where aldehydes are formed when the fatty acids in frying oil break down.

Figure 3 illustrates that the alcohols were present at a lower percentage of 3.8% in pyrolysis oil from pyrolysis of EFB at 500°C. However, the alcohols were reduced to 1.0% and 2.1% at 400°C and 500°C respectively for co-pyrolysis of EFB and UPCO samples and vanished in pyrolysis oil at 500 to 700°C. This could be due to the synergistic influence of UPCO and increased temperature from 400 to 700°C in the pyrolysis of EFB that had upgraded the small number of alcohols from the pyrolysis of EFB into other compounds. In detail, the pyrolysis reactions are given a higher energy environment by the rising temperature which alcohols may become less thermally stable and more prone to breakdown at higher temperatures.

As depicted in Figure 3, ethers in pyrolysis oil were produced only at 400°C (1.5%) and 450°C (1.3%). Consequently, no ethers were found in the pyrolysis oil at 500 to 700°C. This might be due to the higher energy environment that favours the breakdown of ethers into smaller volatile molecules rather than influenced by UPCO. In detail, ethers may become less thermally stable at this temperature range causing them to disintegrate and then converted into other compounds. Similarly, pyrolysis of EFB also did not generate ethers in pyrolysis oil at 500°C as shown in Figure 3. Thus, it can be concluded that at the temperature of 500°C and above, the pyrolysis of EFB inhibits the production of ethers in pyrolysis oil and UPCO has no significance than temperatures in this reaction pathway.

Xu *et al.* (2023) [25] reported that furans are generally produced from hemicellulose in biomass via pyrolysis at 220 to 315°C. Similarly, in this study, the pyrolysis of EFB without UPCO at 500°C has produced the highest furans in pyrolysis oil at 15.1%. Meanwhile, for co-pyrolysis of EFB and UPCO it was observed that furans in pyrolysis oil were generated at 400°C (3.5%), 450°C (3.7%), 500°C (6.3%) and no production of furans was found at 550 to 700°C. In this case, UPCO has played a crucial role in lowering the furans even at the lowest investigated temperature of 400°C as shown in Figure 3. In other words, it can be stated that the furans can be easily and highly produced at 400°C due to lower degradation temperature but the UPCO has enhanced the cracking of furans into lighter compounds. Thus, it can be concluded that the UPCO had converted the furans from EFB into lighter compounds at lower temperatures. In addition, the increased temperature from 550 to 700°C further enhanced the cracking of furans consistently till no furans in pyrolysis oil.

In a nutshell, an obvious difference in the pyrolysis oil's composition is revealed in the comparative research of EFB alone and EFB coupled with UPCO. The pyrolysis of EFB alone produces a mixture of oxygenated compounds. However, a notable increase in hydrocarbon and ester contents is shown when UPCO is added to the pyrolysis process along with EFB. The presence of UPCO acts as a hydrocarbon enhancer with the help of increased temperature from 400 to 700°C, encouraging the formation of pyrolysis oil with a greater hydrocarbon content. This finding suggests that compared to EFB alone, the combination of EFB with UPCO gives considerable advantages in terms of hydrocarbon output. Thus, the determination of the type of hydrocarbons is also important to be known to categorise it by applications and the benefit of applying UPCO in the pyrolysis of EFB.

3.3 Hydrocarbons vs Pyrolysis Oil

The percentage of pyrolysis oil and hydrocarbons in pyrolysis oil were plotted as shown in Figure 4 for a better visualization of the possibility of scaling up this process. It can be observed that the pyrolysis oil was produced in the range of 30.9 to 44.4 wt.% at all temperatures. The differences in the pyrolysis oil yield at all temperatures are insignificant compared to the hydrocarbon yield in pyrolysis oil. For example, although the pyrolysis oil yield at 650°C and 700°C is slightly lower than 550°C and 600°C, but the hydrocarbon percentage are higher, making it a more beneficial fuel. Meanwhile, the temperature at 400 to 500°C favours high pyrolysis oil yield but does not favour the high production of hydrocarbons as depicted in Figure 4.

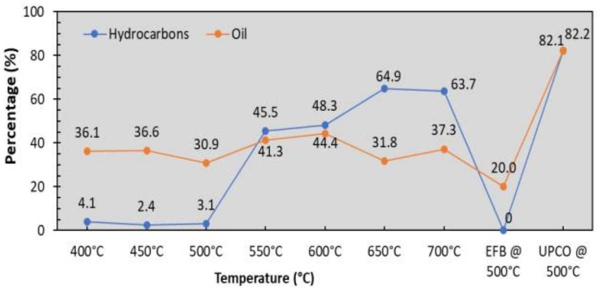


Figure 4 Pyrolysis oil yield vs. hydrocarbon compositions in pyrolysis oil

Thus, in future, for optimization work, the co-pyrolysis of EFB and UPCO should be focused between 550 to 650°C. Apart from that, applying catalysts in the co-pyrolysis of EFB and UCO might produce higher hydrocarbons at a lower temperature range.

3.4 Types of Hydrocarbons in Pyrolysis Oil

Hydrocarbons in pyrolysis oil obtained at 400 to 700°C were divided by carbon numbers ranging from C_5 to C_{24} as shown in Figure 5. It can be observed that light hydrocarbons such as C_5 (0.52%), C_7 (1.0%), C_8 (0.45%), and C_9 (0.98%) were produced at 400°C, 500°C, 450°C, and 550°C respectively and no C_6 hydrocarbons were observed at all temperatures. In detail, monocyclic aromatic hydrocarbons such as p-xylene (C_8H_{10}) were only observed at 450°C. Meanwhile, the rest of the light hydrocarbons can be categorised as alkane and alkene types of hydrocarbons. However, this percentage can be considered very low (≤1%). Thus, it can be concluded that the UPCO did not favour the production of light hydrocarbons (C_5 to C_9) in pyrolysis oil at 400 to 700°C. In other words, UPCO has enhanced the production of hydrocarbons, which consists mainly of medium and heavy hydrocarbons ($\geq C_{10}$). Interestingly, only C_{10} hydrocarbons were observed at all investigated temperatures with the highest at 550°C (1.17%) and 600°C (1.17%) followed by 400°C (0.87%), 500°C (0.65%), 700°C (0.52%), 450°C (0.47%) and 650°C (0.45%). Similarly, C_{10} hydrocarbons at all investigated temperatures can also be considered very low amounts upgraded by UPCO.

Remarkably, higher hydrocarbons were observed starting from C_{11} onwards as shown in Figure 5. In addition, C_{11} hydrocarbons were only produced at 550 to 700°C in the range of 2.6–3.3% which is higher than C_5 to C_{10} hydrocarbons. A similar pattern was observed for C_{12} to C_{17} hydrocarbons at 550 to 700°C. Meanwhile, a fluctuating pattern was seen at 400 to 500°C for C_{12} to C_{17} hydrocarbons. For example, at 400°C, only C_{14} and C_{15} were found at 1.2% and 1.5% respectively followed by at 450°C and 500°C where only C_{15} and C_{14} were observed at 1.0% and 1.5% respectively. Next, it was observed that C_{19} to C_{24} type hydrocarbons were not produced at 400 to 500°C. This might be due to the lower energy environment at these temperatures that has the lower cracking activity of upgrading oxygenated vapours from EFB into hydrocarbons. In addition, C_{21} hydrocarbons were only observed at 550°C (4.8%), 600°C (6.2%) and 700°C (7.8%).

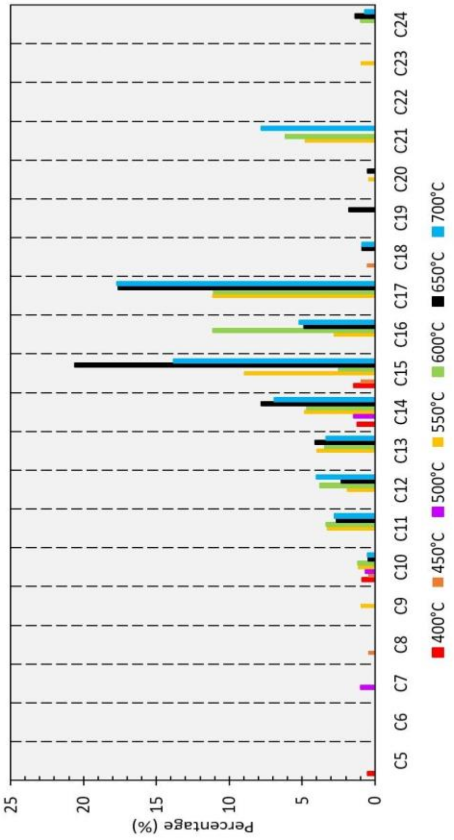


Figure 5 C_5 to C_{24} hydrocarbons type in pyrolysis oil at 400 to 700°C

Hydrocarbon types in pyrolysis oil at 650°C and 700°C were compared side-by-side due to the highest total hydrocarbons in pyrolysis oil. Based on Figure 5, it was found that almost similar amounts of C_{10} to C_{18} hydrocarbons were present in pyrolysis oil except for C_{15} hydrocarbons higher at 650°C. Pentadecane ($C_{15}H_{32}$) was one of the major contributors to the highest total hydrocarbons in pyrolysis oil at 550°C (7.74%), 650°C (10.76%) and 700°C (10.46%). Other than that, 1-Heptadecene ($C_{17}H_{34}$) is the major hydrocarbon product at 550°C (9.34%), 600°C (8.84%), 650°C (14.76%) and 700°C (14.83%). Overall, the UPCO played a significant role in producing a variety of hydrocarbons in pyrolysis oil with an increase in temperature specifically starting from 550°C to 700°C.

4.0 CONCLUSION

The co-pyrolysis of EFB and UPCO into hydrocarbon fuel production at varied temperatures from 400 to 700°C was successfully achieved via a fixed-bed reactor. The results proved that the UPCO has improved the pyrolysis oil yield from pyrolysis of EFB at all investigated temperatures (400-700°C) compared to pyrolysis of EFB only. UPCO also significantly boosts the hydrocarbons and lowers the oxygenated compounds in pyrolysis oil from the pyrolysis of EFB at a temperature range of 550 to 700°C. The highest hydrocarbon yield in pyrolysis oil was achieved at 650°C (64.9%) with oxygenated compounds at 35.1%. Pyrolysis of EFB produces no hydrocarbons in pyrolysis oil with 100% oxygenated compounds. UPCO favours heavy hydrocarbons (C_{10} to C_{17}) rather than light hydrocarbons (C_5 to C_9) in pyrolysis oil at 400 to 700°C. The results obtained in this work show that by a convenient selection of temperature and the synergistic properties of UPCO, it is possible to boost the hydrocarbon yield by lowering the oxygenated compounds in pyrolysis oil. Overall, this study advances the bioenergy field and addresses pressing issues related to waste management and renewable energy production.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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