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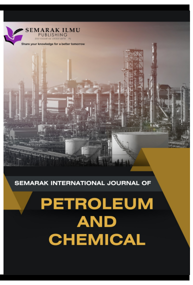

Thermodynamic Analysis of Naphthyl Compounds by Pyrolysis to Hydrogen

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ABSTRACT

Hydrogen (H_2) is a clean and versatile energy carrier with wide-ranging applications across various technologies and industries. It can be produced through several pathways, including fossil fuels, renewable resources, nuclear energy, and chemical processes. In line with efforts to support sustainable development and effective waste management, this study focuses on the production of hydrogen through pyrolysis of refinery waste, specifically fuel oil blended stock (FOBS). A thermodynamic assessment was carried out to evaluate the feasibility of hydrogen generation from this waste material. Naphthalene and 2-methylnaphthalene two dominant polycyclic aromatic hydrocarbons (PAHs) found in FOBS, were selected as representative compounds of FOBS for the modelling process. Using HSC Chemistry 6.0 software, the study applied the Gibbs free energy minimization method to simulate pyrolysis reactions across a temperature range of 273-1273 K at atmospheric pressure (1 bar). Various molar feed ratios of naphthalene to 2-methylnaphthalene were tested: 0.95:0.05, 0.8:0.2, 0.75:0.25, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.25:0.75, 0.2:0.8, and 0.05:0.95. The results indicated that hydrogen production was negligible below 500 K, but increased sharply between 673-1273 K, with the highest yield observed at higher 2-methylnaphthalene content, attributed to enhanced side-chain reactivity and dealkylation behaviour. In contrast to initial assumptions, 2-methylnaphthalene contributed more significantly to hydrogen formation than naphthalene, which primarily acted as a structural backbone during pyrolysis. These findings demonstrate the potential of FOBS as an effective feedstock for hydrogen production and at the same time parallel to a sustainable approach for clean energy generation and industrial waste reduction.

1. Introduction

Hydrogen has emerged as a central focus in the global pursuit of sustainable and low-emission energy solutions. As an energy carrier, hydrogen offers several compelling advantages that make it a key component in future energy systems. One of its most important attributes is that it produces only water vapour when used in fuel cells or combustion processes, thereby eliminating the emission of

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carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter. Contrary to pollutants that are commonly associated with the use of fossil fuels. This clean combustion profile makes hydrogen particularly attractive in the context of international efforts to mitigate climate change and reduce environmental pollution.

In addition to its environmental benefits, hydrogen possesses a high gravimetric energy density, approximately 120 MJ/kg which is significantly greater than that of traditional hydrocarbon fuels [1]. This makes it suitable for high-efficiency energy storage and transport applications. Furthermore, hydrogen is extremely versatile and can be used in a wide range of sectors, including power generation, transportation, chemical manufacturing, steel production, and as a feedstock for ammonia and methanol synthesis [2]. Its compatibility with renewable energy sources also enhances its role in balancing intermittent power supply from solar and wind energy.

Given these advantages, the development of efficient, low-cost, and environmentally friendly hydrogen production methods has become a major research priority. While current commercial hydrogen production is dominated by steam methane reforming, this process is carbon-intensive and undermines the sustainability goal. Therefore, alternative pathways such as pyrolysis of waste materials and biomass are being extensively explored to produce hydrogen with lower environmental impact. The production of hydrogen from waste sources is able to reduce our dependence on fossil fuel energy sources, which cause serious environmental pollution [3]. Retreating waste source to H_2-rich gas is a promising route for the production of hydrogen in this research, the thermochemical conversion of refinery waste, particularly aromatic-rich fractions such as fuel oil blended stock (FOBS), presents a promising opportunity for sustainable hydrogen production.

Fuel oil blended stock (FOBS) is typically regarded as an undesirable by-product of petroleum refining processes and is commonly directed to waste storage due to its complex and unstable composition [4]. FOBS contains a mixture of heavy hydrocarbon compounds, typically toxic and potentially hazardous. Its reactive nature and risk of flammability or explosion require careful handling and secure storage, further emphasizing its classification as industrial waste. Despite these concerns, previous studies have indicated that petroleum residues such as FOBS can contain up to 30% recoverable oil, suggesting potential for energy recovery if treated appropriately [5].

In industrial settings, the recovery of usable oil from such residues is often limited by the complexity and duration of existing treatment processes. However, the growing need for sustainable waste management and alternative energy sources justifies the exploration of more efficient and environmentally friendly methods. This study considers the thermochemical conversion of FOBS specifically through pyrolysis as a viable approach to generate hydrogen while addressing waste accumulation issues. The relevance of this approach is reinforced by the significant volume of FOBS generated in refining operations. In Malaysia alone, petroleum refineries with a processing capacity of approximately 400,000 litres per day are reported to produce around 45,000 litres of FOBS annually [6]. Therefore, the successful conversion of FOBS into hydrogen not only contributes to meeting the growing demand for clean energy but also provides a practical solution to reduce hazardous waste and improve refinery waste management systems.

For evaluating the performance of FOBS undergoing the pyrolysis process to produce hydrogen products a thorough thermodynamic analysis is essential to assess the potential of FOBS as a feedstock for hydrogen production. While earlier studies have explored the thermodynamic behaviour of FOBS through oxidative cracking [4,7]. This method presents notable drawbacks due to the highly mixed and unstable nature of FOBS, the introduction of oxygen in the system increases the risk of violent reactions and explosion hazards. Additionally, oxidative conditions often lead to the formation of oxygenated by-products, which are energetically less favourable and reduce the overall hydrogen yield. Through these limitations, pyrolysis emerges as a more appropriate conversion route for FOBS. As a thermal decomposition process that operates in the absence or near absence of oxygen, pyrolysis significantly reduces safety risks while allowing greater control over product distribution. It is particularly suited for breaking down complex hydrocarbon mixtures such as those found in refinery residues. Despite the industrial relevance of this approach, limited data is currently available on the thermodynamic performance of FOBS under pyrolysis conditions. This research, therefore, aims to fill that knowledge gap by modelling the pyrolytic behaviour of selected naphthyl compounds representative of FOBS, thereby advancing the understanding of its potential in sustainable hydrogen production.

In this study, naphthalene ($C_{10}H_8$) and 2-methylnaphthalene ($C_{11}H_{10}$) were selected as model compounds to represent the aromatic constituents commonly found in FOBS. These two compounds are polycyclic aromatic hydrocarbons (PAHs) that are widely recognized for their abundance in petroleum residues and their stability under storage conditions. Structurally, naphthalene consists of two fused benzene rings, while 2-methylnaphthalene contains an additional methyl group that slightly alters its reactivity and pyrolysis behaviour. Both compounds are characterized by a high carbon and hydrogen content, making them promising candidates for hydrogen production through thermal decomposition.

Under pyrolysis conditions, these aromatic hydrocarbons undergo bond scission and rearrangement reactions that lead to the formation of lighter gases, including hydrogen (H_2), methane (CH_4), carbon monoxide (CO), and other small hydrocarbons. The potential for hydrogen generation is particularly significant, as the aromatic rings in these compounds offer multiple hydrogen atoms that can be liberated under high-temperature conditions, especially when ring-opening and dehydrogenation reactions are favoured. To explore this potential, the Gibbs free energy minimization method was employed using HSC Chemistry 6.0 software, simulating pyrolysis reactions across a wide temperature range (273-1273 K) at atmospheric pressure (1 bar). The equilibrium compositions were determined using the Gibbs free energy minimization method. This approach demonstrates that, under constant temperature and pressure, irreversible processes lead to a reduction in the system's total Gibbs energy. At equilibrium, the total Gibbs free energy reaches its minimum, and its differential becomes zero under these conditions [7]. This modelling approach allows for a systematic investigation into how different operating parameters affect hydrogen production particularly temperature and the molar feed ratio of naphthalene to 2-methylnaphthalene which then influences the equilibrium composition of gaseous products. By evaluating the thermodynamic favourability of hydrogen production and identifying optimal conditions, this study contributes to a deeper understanding of how specific components of FOBS can be harnessed for clean energy generation. Ultimately, such analysis supports the development of sustainable waste-to-hydrogen conversion technologies and promotes better utilization of hazardous refinery by-products.

2. Methodology

A fundamental study of production H_2 by using pyrolysis by setting FOBS as a feedstock of the process was carried on by the thermodynamic computational study field. The thermodynamic study was done in order to implement the postulation data upon the possibility of H_2 able to be produced by using pyrolysis and waste source. This method identifies the dominant component in FOBS to present FOBS in thermodynamic analysis. Parameters considered in this study include temperature, pressure and feed ratio. Then in the Gibbs routine, the calculation for equilibrium composition is employed by using the Gibbs free energy minimization method. The details on the thermodynamic stage of work were disclosed in the following sub-sections.

2.1 Model Compounds of Naphthalene and 2-Methyl Naphthalene

Due to the complex and undefined composition of FOBS, this study adopts a modelling approach by selecting representative compounds that reflect its major aromatic constituents. Based on literature findings and compositional analyses of petroleum residues, naphthalene ($C_{10}H_8$) and 2-methylnaphthalene ($C_{11}H_{10}$) were chosen as surrogate compounds to simulate the thermodynamic behaviour of FOBS under pyrolysis conditions. Naphthalene is a simple polycyclic aromatic hydrocarbon consisting of two fused benzene rings and is frequently found in heavy oil fractions and tar-like substances. It is thermally stable and well-characterized, making it a reliable model for equilibrium calculations. 2-methylnaphthalene, a methylated derivative of naphthalene, introduces slight structural variation and reflects the alkylated aromatic content commonly present in FOBS. The inclusion of this compound allows the study to assess how the presence of methyl side groups may influence pyrolysis behaviour and product distribution.

The selection of these two compounds enables a simplified yet meaningful representation of FOBS in a thermodynamic framework. By varying their molar ratios in the feed from highly naphthalene-dominant to highly 2-methylnaphthalene-dominant. The model captures a range of aromatic content that could reasonably be expected in actual refinery waste streams. These controlled inputs allow for a systematic study of how feed composition impacts the equilibrium formation of hydrogen and other gaseous by-products under different thermal conditions.

2.2 Thermodynamic Analysis

In this study, all the reactions are assumed to be in thermodynamic equilibrium at the exit of the reactor. This assumption allows for the prediction of product distribution based on energy minimization principles without requiring kinetic data. The analysis was conducted using HSC Chemistry 6.0 software, which employs the Gibbs free energy minimization method to calculate the equilibrium composition of reaction products.

The simulation was performed over a temperature range of 273 K to 1273 K, at a constant atmospheric pressure of 1 bar. These conditions were selected to reflect a wide thermal spectrum, including low, moderate, and high-temperature pyrolysis regimes. The pressure was kept constant to isolate temperature and feed composition as the primary variables influencing product formation. A series of nine molar feed ratios of naphthalene to 2-methylnaphthalene were investigated, as shown in

Table **1**. These ratios were designed to assess how varying aromatic content affects the generation of hydrogen and other pyrolysis gases and to determine the optimal blend for maximum H_2 yield.

Table 1
Naphthalene: 2-methylnaphthalene ratio

Naphthalene	2-methylnaphtalene
0.95	0.05
0.80	0.20
0.75	0.25
0.60	0.40
0.50	0.50
0.40	0.60

0.25	0.75
0.20	0.80
0.05	0.95

Each feed ratio was simulated across the entire temperature range to evaluate the equilibrium distribution of pyrolysis products. The Gibbs free energy minimization method within HSC Chemistry 6.0 calculated the equilibrium concentrations of major gaseous species, including hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), as well as minor light hydrocarbons. By examining these outcomes, the study aims to determine the optimal conditions that favour maximum hydrogen production and reduced formation of less desirable by-products. This thermodynamic analysis acts as a theoretical framework to assess the conversion potential of FOBS into hydrogen-rich gas products. Besides, a better understanding of how feedstock composition and pyrolysis temperature influence product distribution can be discovered throughout this study.

2.3 Thermodynamic Equation

HSC Chemistry is a widely used integrated thermodynamic database that offers powerful computational tools for analysing how various reaction parameters influence a chemical system under equilibrium conditions. Using Gibbs free energy minimization, a fundamental principle applied within HSC Chemistry 6.0 to predict equilibrium product distributions. This approach determines the most stable state of a chemical system by minimizing the total Gibbs free energy (G) of all participating species under specified conditions of temperature and pressure.

The spontaneity of a chemical reaction is determined by the change in Gibbs free energy(ΔG). A negative ΔG indicates that the reaction is thermodynamically favourable and proceeds spontaneously, whereas a positive ΔG suggests that the reaction is non-spontaneous under standard conditions. The general relationship is expressed in Eq. (1):

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where:

ΔG: Gibbs free energy change (J/mol)
ΔH: Enthalpy change (J/mol)
T: Absolute temperature (K)
ΔS: Entropy change (J/mol·K)

This equation illustrates how both enthalpy and entropy affect the feasibility of a chemical reaction. In pyrolysis reactions, where heat input is required to break chemical bonds, temperature becomes a significant factor influencing ΔG. A previous study stated that a more negative ΔG value corresponds to a greater likelihood that the reaction will proceed without external intervention [8]. In this study, calculating ΔG across a wide temperature range provides the thermodynamic favourability of hydrogen production from naphthalene and 2-methylnaphthalene. This forms the theoretical basis for selecting optimal pyrolysis conditions in waste-to-hydrogen conversion processes.

3. Results and Discussions

3.1 Equilibrium Constant and Possible Reaction Pathways

The thermodynamic behaviour of naphthalene ($C_{10}H_8$) and 2-methylnaphthalene ($C_{11}H_{10}$) under pyrolysis conditions plays a critical role in evaluating their viability for hydrogen (H_2) production.

These polycyclic aromatic hydrocarbons (PAHs), commonly found in refinery by-products such as FOBS, undergo a series of complex chemical transformations at elevated temperatures, particularly within the range of 273 K to 1273 K under inert or oxygen-deficient conditions.

In this study, the main pyrolysis reactions include thermal cracking, intermediate cracking, dehydrogenation, and secondary reforming. As summarized in **Table 2**, the thermal cracking of naphthalene primarily leads to smaller aromatic and unsaturated hydrocarbons. The possible reaction for naphthalene to crack into smaller hydrocarbons (C_xH_y), syngas (CO_2, CO, H_2, CH_4), water or vapour and also carbon (R1) which probably as a solid residue. The naphthalene may also possibly decompose into benzene (C_6H_6), acetylene (C_2H_2), and ethylene (C_2H_4) (R2), or form phenylacetylene (C_8H_6) and acetylene (C_2H_2) (R3), reflecting typical ring-fragmentation pathways. Additionally, intermediate species such as C_7H_6 and propyne (C_3H_2) (R4) may form through further breakdown of the aromatic system.

At higher temperatures, dehydrogenation (R5) becomes more favourable, leading to the release of molecular hydrogen (H_2) via the removal of hydrogen atoms from the aromatic rings. Simultaneously, carbonization or coke formation (R6) may occur, converting aromatic compounds into solid carbon while releasing additional H_2, this behaviour is typical of heavy aromatics under severe thermal conditions. Free hydrogen radicals may also recombine (R7) to form H_2 gas.

For 2-methylnaphthalene ($C_{11}H_{10}$), two principal reaction pathways are considered. It may undergo thermal cracking (R8), producing phenylacetylene (C_8H_6), methane (CH_4), and acetylene (C_2H_2). Alternatively, it may follow a dealkylation route (R9), forming naphthalene and methane. These reactions indirectly contribute to H_2 production by generating smaller hydrocarbons that can undergo secondary reforming.

Water vapour, expected to be present due to the decomposition of oxygenated compounds in FOBS, can enable additional gas-phase reactions that further enhance hydrogen yield. These include the steam reforming of methane (R10), the water-gas shift reaction (R11), and methanation (R12). Secondary hydrogenation reactions, such as the conversion of acetylene (C_2H_2) to ethylene (C_2H_4) (R13), may also occur, though they are generally less favoured under high-temperature pyrolysis conditions. The repeatability of ethylene (C_2H_4) to form ethane (C_2H_6) (R14) and butene (C_4H_8) to butane (C_4H_{10}) (R15) is also higher. In summary, this complex network of reactions demonstrates the thermodynamic feasibility of hydrogen production from aromatic-rich refinery waste, with naphthalene and 2-methylnaphthalene serving as effective model compounds.

Table 2
Possible reaction of Naphthalene ($C_{10}H_8$) and 2-methylnaphthalene ($C_{11}H_{10}$) under pyrolysis conditions

Reaction	Type of reaction	Equation
R1	Thermal cracking	$C_{10}H_8 \rightarrow C_xH_y + CO_2 + CO + H_2 + CH_4 + H_2O + C$
R2	Thermal cracking	$C_{10}H_8 \rightarrow C_6H_6 + C_2H_2 + C_2H_4$
R3	Thermal cracking	$C_{10}H_8 \rightarrow C_8H_6 + C_2H_2$
R4	Intermediate cracking	$C_{10}H_8 \rightarrow C_7H_6 + C_3H_2$
R5	Dehydrogenation	$C_{10}H_8 \rightarrow C_{10}H_6 + H_2$
R6	Carbonization (Polymerization)	$C_{10}H_8 \rightarrow 10C\ (solid) + 4H_2$
R7	Radical H2 evolution	$2H\cdot \rightarrow H_2$
R8	2-methylnaphthalene cracking	$C_{11}H_{10} \rightarrow C_8H_6 + CH_4 + C_2H_2$
R9	2-methyl naphthalene dealkylation	$C_{11}H_{10} \rightarrow C_{10}H_8 + CH_4$
R10	Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$
R11	Water gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$
R12	Methanation	$CO + 3H_2 \leftrightarrow CH_4 + H2O$
R13	Hydrogenation	$C_2H_2 + H_2 \rightarrow C_2H_4$
R14	Hydrogenation	$C_2H_4 + H_2 \rightarrow C_2H_6$

R15	Hydrogenation	$C_3H_6 + H_2 \rightarrow C_3H_8$

3.2 Effects of Temperature and Feed Ratio on Gas Products at 1 Bar

Error! Reference source not found. (a) illustrates the thermodynamic simulation results for hydrogen (H_2) production from various feed ratios of naphthalene ($C_{10}H_8$) and 2-methylnaphthalene ($C_{11}H_{10}$) over a temperature range of 273 K to 1273 K, under atmospheric pressure (1 bar). The feed composition was systematically varied from 0.95:0.05 to 0.05:0.95 to examine the impact of alkyl substitution on hydrogen evolution.

At low temperatures below 500K, all feed ratios show negligible hydrogen production. This observation is consistent with the high thermal stability of polycyclic aromatic hydrocarbons (PAHs), which require higher activation energy for bond cleavage and radical formation [9]. In the intermediate temperature at the range of 573–873 K, a sharp increase in hydrogen production is observed across all feed ratios. This marks the onset of significant pyrolytic reactions such as ring-opening, side-chain cracking, dealkylation, and aromatic dehydrogenation [10]. These transformations contribute to the formation of molecular hydrogen and smaller hydrocarbon fragments. At high temperatures with a range of 973–1273 K, hydrogen production reaches a plateau, suggesting near-complete conversion or equilibrium-limited yields. Secondary gas-phase reactions such as steam reforming of methane and the water-gas shift reaction (WGSR) possibly contribute to sustaining hydrogen output, particularly when moisture or oxygenated species are present in the feed [11].

While feed composition significantly influences hydrogen yield. Formulations with higher 2-methylnaphthalene content such as 0.05:0.95 and 0.2:0.8, consistently demonstrate greater hydrogen production. The presence of a methyl substituent not only increases the hydrogen-to-carbon ratio but also enhances chemical reactivity by facilitating dealkylation and side-chain scission [12]. Conversely, naphthalene-rich mixtures such as at a ratio of 0.95:0.05 resulted in lower hydrogen yields due to their higher aromatic stability and lower inherent hydrogen content.

The mid ratio of naphthalene:2-methylnaphthalene complemented the result as ratios 0.6:0.4 and 0.5:0.5 yield moderate H_2 output but keep peaking at a ratio of 0.4:0.6. Generally, can conclude that naphthalene contributes structural integrity and carbon skeletons for secondary reactions, while 2-methylnaphthalene enhances hydrogen availability through side-group reactions. But in general, temperature was the main indicator as the primary driver of hydrogen production, with optimal yields achieved between 673 K and 1273 K. The feed ratio plays a complementary role, with higher 2-methylnaphthalene content enhancing hydrogen output.

The thermodynamic equilibrium of H_2 production demonstrates a strong dependence on both reaction temperature and the feed ratio of naphthalene ($C_{10}H_8$) to 2-methylnaphthalene ($C_{11}H_{10}$) under atmospheric pressure (1 bar). Simultaneously, the behaviour of methane (CH_4) production, as presented in **Error! Reference source not found.** (b), reveals that CH_4 formation is relatively high at lower temperatures (below 673 K), approximately 2.0-2.5 kmol across all feed ratios. However, its concentration declines sharply beyond 673 K and approaches near-zero values at temperatures exceeding 1173 K. This significant reduction in CH_4 correlates with the activation of steam reforming ($CH_4 + H_2O \rightarrow CO + 3H_2$) in R10, which consumes CH_4 and contributes directly to the observed increase in hydrogen levels at elevated temperatures [13].

The inverse relationship between CH_4 and H_2 yields reinforces the thermodynamic prediction that methane behaves as a reactive intermediate. Under high-temperature conditions, CH_4 undergoes endothermic cracking and reforming reactions that release additional hydrogen. This trend is especially pronounced in feedstocks with higher proportions of 2-methylnaphthalene, which contain an alkyl substituent that enhances CH_4 formation at lower temperatures. These methyl groups are more labile and readily cleaved, generating CH_4 as an early decomposition product [14]. As temperatures rise, the system favours the conversion of this CH_4 into H_2, particularly through steam reforming and water-gas shift reactions [15]. Therefore, feed compositions rich in 2-methylnaphthalene not only yield more CH_4 initially but also enable more efficient downstream hydrogen production, enhancing the overall H_2 output.

Error! Reference source not found. (c) presents the reaction behaviour by tracking acetylene (C_2H_2) formation across the temperature range. As an intermediate commonly produced during the high-temperature pyrolysis of aromatic compounds, C_2H_2 typically emerges from ring-opening or side-chain cracking processes. The trend of C_2H_2 production peaking when temperature beyond 1073 K. This pattern suggests that acetylene forms most readily under partial cracking conditions and is especially prominent when 2-methylnaphthalene is present, likely due to the influence of the methyl group in promoting ring fragmentation and the formation of unsaturated fragments [14]. Feedstocks with a higher ratio of 2-methylnaphthalene tend to yield slightly more C_2H_2, which proves the idea that methyl-substituted aromatics are more prone to producing reactive intermediates during thermal decomposition. The formation of C_2H_2 undergoes hydrogenation in R12 and contributes towards the formation of ethylene (C_2H_4).

In complement to the C_2H_2 trend, **Error! Reference source not found.** (d) revealed a progressive increase in ethylene (C_2H_4) production with rising temperature, showing a sharp uptrend beyond 773 K and reaching a maximum near 1273 K. This behaviour of C_2H_2, reinforces the idea that C_2H_2 serves as an intermediate for formation of C_2H_4. As temperatures rise, acetylene undergoes further transformation, likely through hydrogenation and radical-induced reactions, leading to more thermodynamically stable products like C_2H_4. The steady increase across all feed ratios also indicates that the formation of C_2H_4 is more governed by temperature than by feedstock composition. However, mixtures with higher 2-methylnaphthalene content tend to show marginally higher C_2H_4 yields.

Error! Reference source not found. (e) and (f), which depict the production trends of ethane (C_2H_6) and propane (C_3H_8), respectively, across the same temperature range. Both compounds exhibit a clear bell-shaped curve, with formation increasing notably between 573 K and peaking around 773 K, before declining steadily as the temperature continues to rise. Based on this result, the saturated hydrocarbons are considered primarily intermediate products formed during the early and mid stages of thermal cracking. The moderate temperatures favour the formation of smaller saturated molecules through radical recombination and hydrogenation of lighter unsaturated fragments. In particular, ethane is likely formed from the hydrogenation of ethylene or methyl radicals, while propane may originate from the coupling of methyl and ethyl fragments or dealkylation reactions involving side chains from 2-methylnaphthalene. These reactions are most prominent at intermediate temperatures, aligning with the observed peaks in **Error! Reference source not found.** (e) and (f).

At higher temperatures beyond 873 K, both C_2H_6 and C_3H_8 begin to decline significantly. This reduction is consistent with the onset of secondary reactions, such as thermal cracking and reforming, which convert these relatively stable alkanes into lighter gases like H_2 and CO. The decline also coincides with the increase in hydrogen and ethylene production, indicating a shift toward dehydrogenation pathways and further breakdown of intermediates under more severe conditions [15].

Feed composition showed it plays a subtle but important role. Mixtures higher in 2-methylnaphthalene tend to produce slightly more C_2H_6 and C_3H_8, particularly around the peak temperature. This is likely due to the presence of methyl groups, which are more labile and readily cleaved, contributing to the formation of small alkyl radicals during the initial stages of pyrolysis [12, 14]. C_2H_6 and C_3H_8 act as transient intermediates, which are quickly formed and consumed depending on temperature and feedstock composition. Their behaviour indicated the temperature-sensitive nature of pyrolysis reactions and the influence of alkyl substitution on product distribution.

In **Error! Reference source not found.** (g), propene (C_3H_6) production was negligible at temperatures below 673 K, reflecting the thermal stability of the polycyclic aromatic feedstocks and the need for higher energy to initiate cracking reactions. A sharp increase in C_3H_6 formation occurs between 773 K and 1073 K, marking the active decomposition zone where side-chain scission, dealkylation, and ring-opening reactions dominate. This trend is specifically observed when mixtures rich in 2-methylnaphthalene such as at ratios 0.2:0.8 and 0.05:0.95, the possibility of methyl substituent facilitates fragmentation pathways and increases the availability of three-carbon fragments [12]. These fragments may undergo cracking (R1) to form C_3H_6 and contribute towards the formation of C3H8 [11]. However, due to the low amount of C_3H_6 and involving of a few reactions the formation of C_3H_8 in **Error! Reference source not found.** (f) is also not too high. For feed ratios richer in naphthalene such as 0.95:0.05, it consistently produces lower amounts of C_3H_6. This reflects the higher aromatic stability and lower hydrogen content of naphthalene, which limit its propensity to undergo cracking and radical formation [9].

Similarly, **Error! Reference source not found.** (h) demonstrates that butene (C_4H_8) formation follows a comparable bell-shaped curve, with minimal production at low temperatures and a marked increase between 673 K to 973 K. The trend in C_4H_8 production is also more prominent in 2-methylnaphthalene-dominant mixtures, supporting the role of the methyl group in enhancing molecular breakdown and generating larger olefins [14]. As with C_3H_6, the decline in C_4H_8 above 973 K, might be the C_4H_8 thermal cracking and further dehydrogenation, leading to smaller molecules such as C_2H_2, C_2H_4, and H_2 [15].

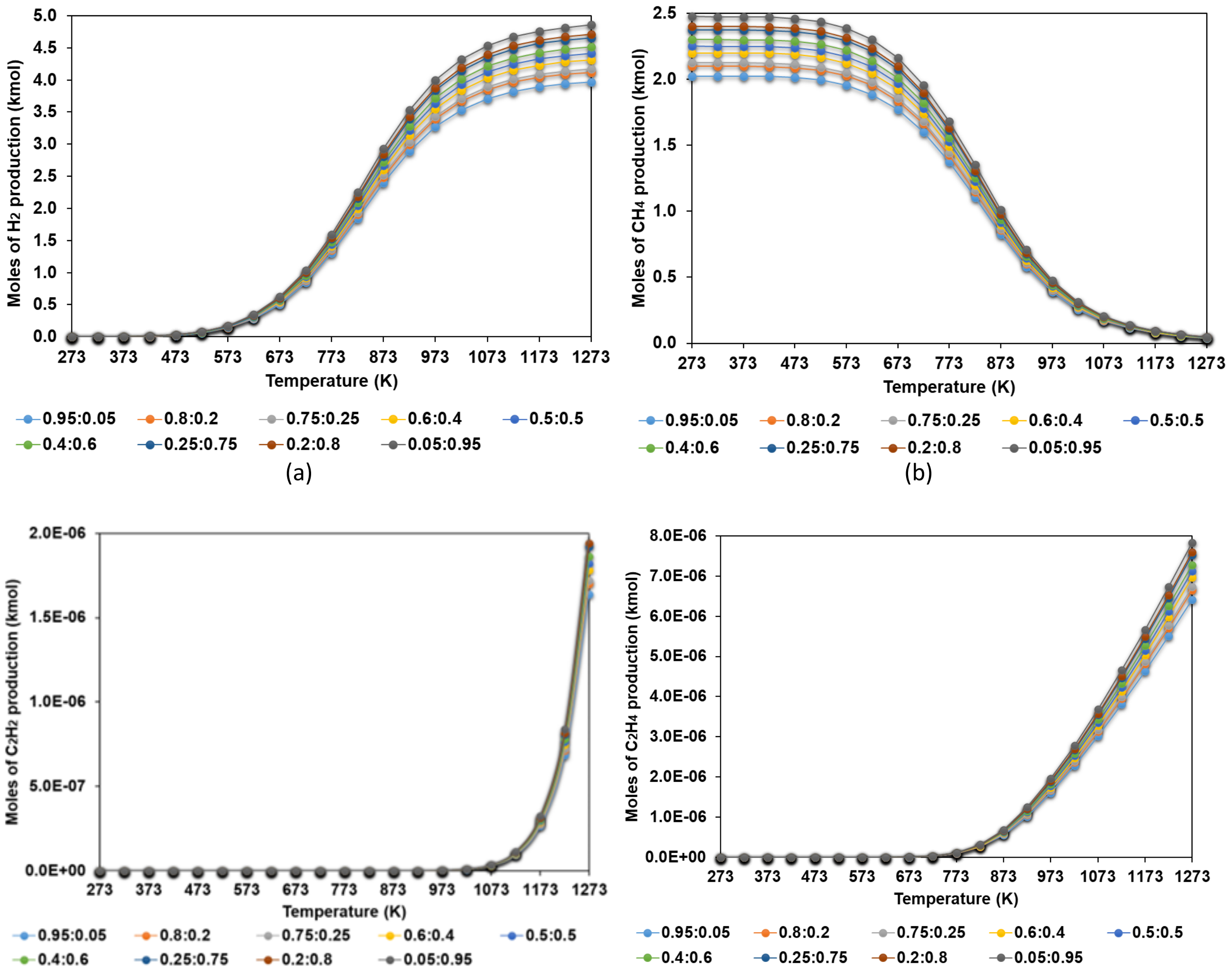
Error! Reference source not found. (i) shows the production pattern of butane (C_4H_{10}), which follows a bell-shaped curve, similar to what is seen for ethane (C_2H_6), propane (C_3H_8), and butene (C_4H_8). At lower temperatures, especially below 573 K, the amount of butane produced is very low. As the temperature rises between 573 K and 773 K, the production increases noticeably. This temperature range seems to support reactions like side-chain hydrogenation, the joining of small alkyl radicals, and the recombination of methyl and ethyl fragments. Among the different feed ratios, mixtures with more 2-methylnaphthalene such as 0.2:0.8 and 0.05:0.95 produce more butane. This suggests that the methyl group in 2-methylnaphthalene helps form the small fragments needed for butane. In contrast, mixtures with more naphthalene like 0.95:0.05 produce less butane, likely because naphthalene has fewer hydrogen atoms and a more stable structure that does not break apart easily.

When the temperature goes beyond 773 K, butane production starts to drop for all feed ratios. This is probably due to further cracking and decomposition, where butane breaks down into smaller gases like ethylene (C_2H_4), acetylene (C_2H_2), methane (CH_4), and hydrogen (H_2). These types of reactions become more common at high temperatures, where more energy is available and radical reactions take over. 2-methylnaphthalene likely contributes to the formation of butane earlier in the reaction by supplying reactive groups, but as the temperature increases, most of these are broken down into simpler gases instead of accumulating as butane.

Error! Reference source not found. (j) presents the trend of carbon formation as a function of temperature across different feed ratios. At lower temperatures, carbon production remains negligible. However, a significant increase is observed once the temperature exceeds 573 K, with the highest carbon yield occurring at 1273 K for all feed compositions. This rise corresponds with the activation of pyrolytic processes such as dehydrogenation, aromatic condensation, and polymerization as the main contributor to solid carbon (C) formation under thermal stress.

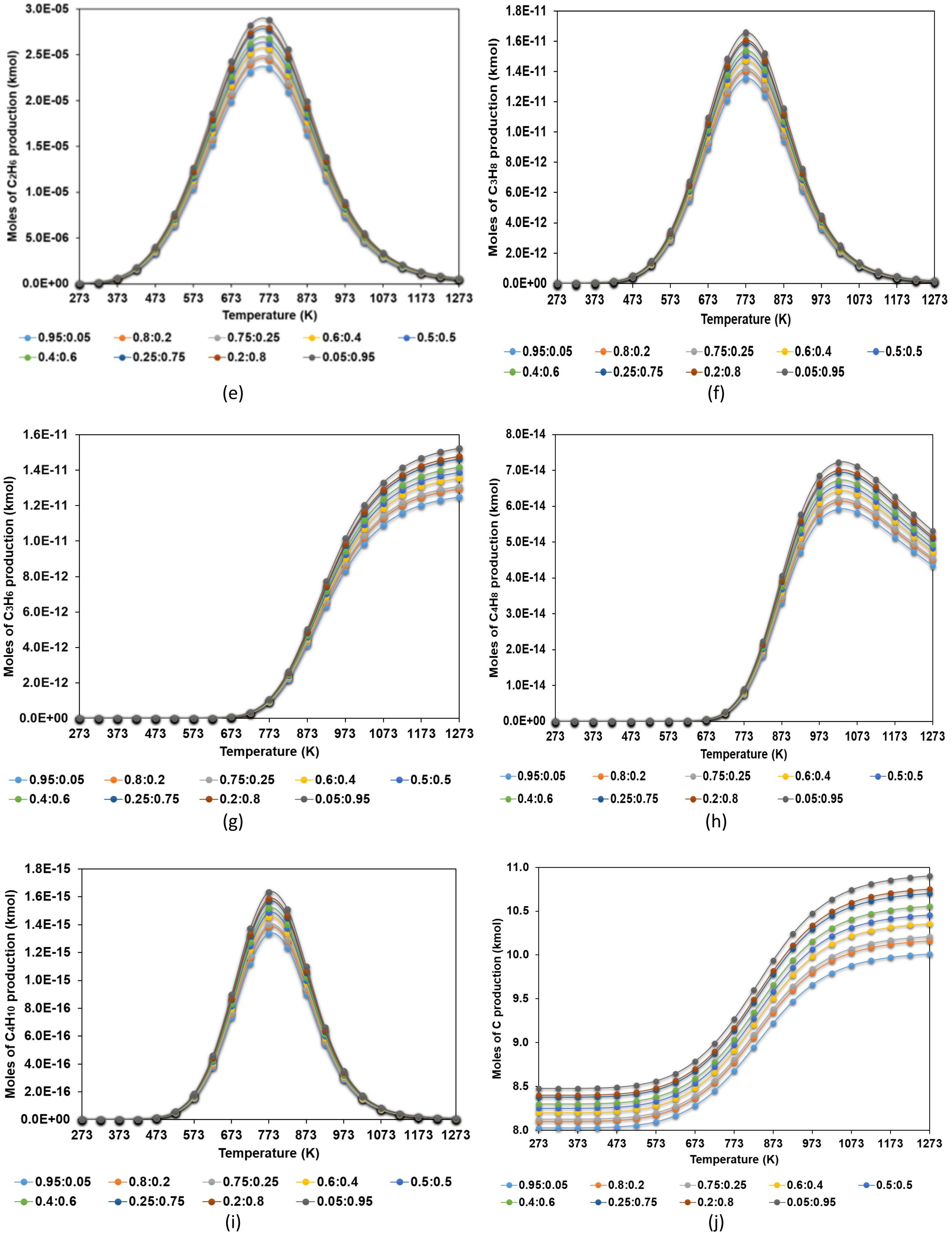
Among the various feed ratios, the 0.05:0.95 mixture produces the most carbon. This outcome showed the influence of alkyl substitution on carbon formation. The methyl group in 2-methylnaphthalene enhances its reactivity compared to unsubstituted naphthalene. Methyl groups are more susceptible to homolytic cleavage, forming reactive radicals that can undergo condensation and cyclization, ultimately leading to the formation of larger polycyclic structures and solid carbon deposits.

In contrast, the naphthalene structure provides greater thermal stability, making it more resistant to bond cleavage and radical generation. As a result, mixtures with higher naphthalene content, such as 0.95:0.05, tend to produce significantly less carbon under similar conditions. The absence of alkyl groups limits the extent of chain branching and heavy molecular growth which both are common pathways toward coke and soot formation. Therefore, while elevated temperature is a primary driver of carbon formation, feed composition particularly the presence of reactive alkyl groups in 2-methylnaphthalene significantly amplifies this tendency. This observation figures out a balance of hydrogen production goals with carbon management were need to be parallel to achieve SDG 11 and SDG 12 goals of building resilient, sustainable urban systems and promoting responsible consumption and production practices.



(a) (b)

(c) (d)



(e) (f) (g) (h) (i) (j)

Fig. 1. The product produced from FOBS under pyrolysis conditions at 273-1273 K: (a) H_2, (b) CH_4, (c) C_2H_2, (d) C_2H_4, (e) C_2H_6, (f) C_3H_8, (g) C_3H_6, (h) C_4H_8, (i) C_4H_{10} and (j) C

3.3 Effect of Feed Ratio on Hydrogen Production

Based on the data presented in **Error! Reference source not found.** (a), the composition of the feed specifically the ratio of naphthalene ($C_{10}H_8$) to 2-methylnaphthalene ($C_{11}H_{10}$) has a clear influence on hydrogen (H_2) production. At temperature 1273 K and atmospheric pressure the hydrogen yield was observed across different feed compositions as all the hydrogen yield peaking at this temperature.

Among the variations of molar ratio, the highest hydrogen production reaching over 4.8 kmol was observed at the feed ratio of 0.05:0.95 (naphthalene:2-methylnaphthalene). This outcome suggests that 2-methylnaphthalene plays a greater role in contributing to H_2 formation under pyrolysis conditions. The presence of a methyl group on the naphthalene ring structure makes 2-methylnaphthalene more susceptible to bond cleavage. This side-chain functional group facilitates radical formation and enhances reactivity during pyrolysis, particularly through dealkylation and C-C bond scission mechanisms that release smaller hydrocarbons and hydrogen gas [16].

In contrast, the feed composition dominated by naphthalene (0.95:0.05) resulted in the lowest hydrogen yield, recorded at below 3.7 kmol. Naphthalene, as a highly stable polycyclic aromatic hydrocarbon, requires higher activation energy for ring-opening reactions, making it less efficient at contributing to H_2 production in the absence of catalytic enhancement. Its limited decomposition pathways reduce the availability of reactive intermediates necessary for hydrogen evolution [17].

Intermediate feed ratios such as 0.6:0.4 and 0.5:0.5 yielded hydrogen amounts in between these two compounds. This pattern indicates that a balanced mixture could offer synergistic effects, where the stability of naphthalene is complemented by the higher reactivity of 2-methylnaphthalene. The methylated compound likely initiates decomposition more readily, while the aromatic backbone of naphthalene stabilizes the reaction environment, promoting secondary gas-phase reactions. The findings figured out that once the proportion of 2-methylnaphthalene exceeds 50%, a threshold effect may be reached, where hydrogen production increases more significantly. This could be attributed to the higher availability of labile hydrogen and radical species, which shift the equilibrium of secondary reactions such as dehydrogenation and steam reforming, enhancing H_2 release.

In conclusion, 2-methylnaphthalene contributes more significantly to hydrogen production under thermal pyrolysis due to its lower thermal stability and the presence of an alkyl side chain that promotes fragmentation. This finding supports the selection of alkylated PAHs as promising model compounds for maximizing hydrogen yields in thermochemical conversion processes of FOBS or for reference to the other waste-based feedstocks.

3.4 Limitation of Thermodynamic Study

Although thermodynamic equilibrium modelling is a powerful tool for exploring the feasibility of hydrogen (H_2) production from polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and 2-methylnaphthalene, it does not fully reflect the complexities of practical pyrolysis systems. These models operate under idealised assumptions such as instantaneous equilibrium, homogeneous temperature distribution, and the absence of mass transfer or kinetic limitations which can oversimplify the actual reaction environment.

Thermodynamic models can indicate the most thermodynamically favoured product distribution but no information on reaction rates or the stability and transformation of intermediate species. In pyrolysis, especially at the molecular level, processes like aromatic ring scission, radical formation, or side-chain dealkylation often require high activation energies. Without sufficient residence time or catalytic facilitation, many of these pathways may not proceed to completion, leading to discrepancies between predicted and observed product yields.

Another limitation lies in the feedstock representation. While naphthalene and 2-methylnaphthalene are significant components of FOBS, the result does not fully represent the full chemical complexity of the material. FOBS contains a wide array of other hydrocarbons such as aromatic and aliphatic as well as oxygenates, nitrogen and sulphur-containing compounds. These constituents can interact in unexpected ways, affecting reaction mechanisms, shifting thermodynamic equilibria, or altering product selectivity.

4. Conclusions

The formation of hydrogen during pyrolysis is primarily driven by temperature, with optimal yields achieved in the range of 673 K to 1273 K. However, feedstock composition significantly influences both the quantity and efficiency of hydrogen generation. 2-methylnaphthalene plays a critical role in enhancing H_2 output through its reactive methyl substituent, which facilitates early-stage bond cleavage, radical formation, and dealkylation. This not only accelerates the release of hydrogen but also promotes secondary gas-phase reactions such as methane reforming and the water-gas shift reaction, both of which contribute further to hydrogen enrichment. However, the same features that boost hydrogen production also increase the likelihood of carbon formation due to condensation and polymerisation of reactive intermediates. Thus, while 2-methylnaphthalene-rich feeds offer better hydrogen yields, they also present challenges in managing carbon deposition.

5. Future recommendations

To overcome the limitations of thermodynamic equilibrium modelling and bring predictions closer to real conditions, future research should consider integrating kinetic aspects into the simulation framework. By considering reaction rates, the formation and behaviour of intermediates, and the effect of residence time, the models would better reflect the actual dynamics occurring during pyrolysis and reforming, especially given the high activation energies involved.

In addition, future work should broaden the scope of model compounds to better represent the complex nature of FOBS. Although naphthalene and 2-methylnaphthalene are among the main components, FOBS consists of a wide variety of chemical species, including aliphatic, oxygenated compounds, and molecules containing nitrogen or sulphur. These additional constituents may influence the reaction pathways and product distribution in ways that binary systems cannot fully capture. Incorporating a more diverse compound set or verifying model predictions through experiments would provide firmer data.

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