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Fuel Oil Blended Stock (FOBS) Valorisation: Thermodynamic Modelling of Pyrolysis to Hydrogen

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Fuel oil blended stock (FOBS) is an accumulation of petroleum-based waste produced by the refinery industry and is often considered an undesirable byproduct. The issues concerning the abundance of FOBS have risen significantly over the past few decades due to continuous petrochemical operations. While various methods, such as recycling and energy recovery, have been implemented to manage FOBS residues, ongoing research is essential to develop more efficient alternatives and enhance existing solutions. A thorough understanding of thermodynamic parameters is crucial for optimizing these processes, as it enables early prediction of process outcomes, identification of potential hazards, and improved energy efficiency through reaction mechanism analysis. This study employs thermodynamic modelling using HSC Chemistry software, applying Gibbs free energy minimization for equilibrium calculations. Naphthalene ($C_{10}H_8$) was selected as the model reactant for pyrolysis to investigate syngas production. The effects of temperature (273 - 1,273 K) and pressure (1 - 50 bar) on equilibrium composition were examined by focusing on hydrogen (H_2) gas as the primary product. The highest H_2 yield, approximately 4.0 kmol was achieved at 1,273 K and 1 bar. The results showed that the production of H_2 was enhanced by the formation CH_4 as an intermediate in hydrogen generation. This novel thermodynamic evaluation of naphthalene that represents FOBS highlighted the potential of this waste material, potentially reinforcing the concept of waste-to-energy conversion.
Keywords: fuel oil blended stock, hydrogen, thermodynamic analysis, FOBS, light hydrocarbon

1. Introduction

Energy consumption is expected to continue rising in response to global population growth and the increasing reliance on technology, both of which drive higher energy demand over time. However, meeting this growing demand is becoming increasingly challenging due to the finite nature of fossil fuel resources. According to Anahas and Muralitharan (2018), the depletion of fossil fuels is closely tied to escalating energy needs, with projections indicating a significant percentage increase in global energy demand by 2,050. These concerns highlight the urgent need to ensure a sustainable energy supply. To address this, alternative energy sources are being explored as potential substitutes for non-renewable fossil fuels, aiming to both meet future energy demands and conserve existing fossil fuel reserves.

In response to the ongoing depletion of fossil fuels, alternative energy sources are being explored to ensure long-term energy sustainability. One such potential source is fuel oil blended stock (FOBS), which has been identified as a viable feedstock for hydrogen (H_2) production to meet future energy demands. According to Ranizang et al. (2024) and Teo et al. (2021), FOBS is a waste residue generated by the refinery industry and is typically regarded as an undesirable byproduct. It is classified as a scheduled waste due to its hazardous nature, containing a mixture of unknown and potentially harmful chemicals. Although proper handling procedures for FOBS are in place, their continuous generation poses environmental challenges, particularly in terms of storage and disposal. These issues not only contribute to environmental degradation but may also have implications for public health. Given these concerns, the utilization of FOBS for energy recovery presents a promising solution for both waste management and sustainable energy production. As a petroleum-derived waste, FOBS is considered a potential feedstock for energy production due to its significant oil content: around 30 % oil, 40 %

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water, and a remaining fraction of solid residues (Kuan et al., 2020). The oil component is a complex blend, likely containing aliphatic and aromatic hydrocarbons (such as n-eicosane, toluene, naphthalene, etc), asphaltenes, and nitrogen-sulphur-oxygen-containing compounds (Huang et al., 2015), reflecting its origin as a petroleum-derived waste.

Due to the presence of oxygenated compounds and various impurities in FOBS, pyrolysis stands out as an effective treatment technique. Since pyrolysis takes place in an oxygen-deficient environment (Ksenia et al., 2022), it provides better control over chemical reactions and final products by reducing the risk of undesirable byproducts. Pyrolysis is a well-established chemical method used to recycle waste into valuable products. The process works by thermally breaking down long hydrocarbon chains into smaller molecules through the application of heat and pressure in an oxygen-free environment. Operating temperatures generally fall within the range of 300 °C to 900 °C. The process results in three main products: liquid, gas and solid (Sivagami, 2022). The gas produced, owing to its high calorific value, is often reused as a heat source within the system, helping to reduce its overall energy consumption (Rajendran et al., 2019). Compared to other thermochemical processes such as combustion and gasification, pyrolysis remains the most effective method for treating FOBS, primarily due to its relatively lower thermal energy demand and its capacity to produce H_2 without requiring an oxidizing environment. While combustion leads to the complete oxidation of the feedstock and gasification yields syngas through partial oxidation, both approaches tend to consume more energy and produce lower H_2 selectivity (Che et al., 2021). In contrast, pyrolysis enables controlled thermal decomposition, facilitating reactions such as thermal cracking, dehydrogenation, and steam reforming that contribute directly to H_2 formation (Foong et al., 2021). This makes pyrolysis a more favorable route for maximizing H_2 yield from FOBS. As FOBS remains in the early stages of exploration, current studies are largely limited to thermodynamic and experimental investigations. Initial research has focused on thermodynamic analysis, using n-eicosane as a model compound for oxidative cracking to produce H_2 (Teo et al., 2021a). Subsequently, Lau et al. (2025) continued the thermodynamic study of oxidative cracking of n-eicosane and toluene to produce H_2. This was followed by experimental studies involving the pyrolysis of FOBS in the presence of catalysts such as Mo/ZSM-5 and Ni/ZSM-5 for H_2 generation (Ranizang et al., 2024). However, given that the research is still at a preliminary stage, significant knowledge gaps remain, and the full potential of FOBS as an alternative energy source has yet to be fully understood. Thermodynamic analysis of n-eicosane and toluene as model compound representing FOBS towards hydrogen has been previously studied, but not yet for naphthalene. Naphthalene is decided as the sole model compound as it was the most dominant species detected from our FOBS analysis using GCMS, yielding 14.7%. Subsequent species were naphthalene 2-methyl (9.93%), naphthalene 1-methyl (6.69%), heptasiloxane tetradecamethyl (4.86%) and others which constitute less than 4% (Ranizang et al., 2025). By studying naphthalene enabled a thermodynamic assessment of hydrogen formation from an aromatic compound, helping to establish a baseline understanding of its pyrolysis behavior. To address this, the present study aims to perform a thermodynamic analysis of FOBS pyrolysis, employing naphthalene as model compound to provide predictive data on H_2 production and proving FOBS of its viability as a sustainable energy feedstock, by employing naphthalene as a model compound.

2. Methodology

This study investigated the thermodynamics of naphthalene pyrolysis using HSC Chemistry version 6.0, applying the total Gibbs free energy minimization approach. The system was evaluated at equilibrium, where all components were allowed to react freely until the system reached the minimum total Gibbs free energy. The research flow was illustrated in Figure 1.

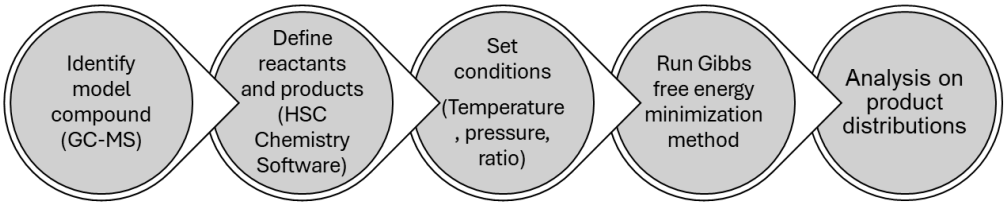

Figure 1: Research flowchart for thermodynamic analysis of H_2 gas under pyrolysis condition

In order to perform this thermodynamic study, FOBS was first analyzed using GC-MS to identify its dominant compounds, which guided the selection of naphthalene as a representative model compound. Naphthalene ($C_{10}H_8$) was the sole reactant, selected as a model compound, and its thermal decomposition yielded major products such as H_2, various C_2-C_4 hydrocarbons (CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}), and solid carbon (C), while minor or trace byproducts were excluded to simplify the model. All the gases species were

assumed to behave as ideal gases and solid carbon was the only species present in the solid phase. The total input was fixed at 1 kmol, with operating temperatures between 273 – 1,273 K and pressures from 1 to 50 bar. Complete conversion of naphthalene was observed across all operating conditions (by assuming equilibrium thermodynamic from Gibbs free energy minimization), confirming the thermodynamic feasibility of its pyrolysis.

3. Results and discussions

3.1 Possible reaction pathways of pyrolysis on FOBS to H_2 generation

The reaction between naphthalene under controlled thermodynamic conditions plays a crucial role in converting FOBS into the production of H_2 gas. In this research, the main pyrolysis reactions of naphthalene involved 15 reactions with the possible type of reaction consisted of thermal cracking (R1, R2, R3), intermediate cracking (R4, R5), dehydrogenation (R6), polymerization (R7), hydrogenation (R8, R9, R10), water gas shift reaction (WGSR) (R11, R13), steam reforming (R12) and methanation (R14, R15). Table 1 summarizes the possible reaction of model compound naphthalene ($C_{10}H_8$) under pyrolysis.

Naphthalene ($C_{10}H_8$) corresponds to a polycyclic aromatic hydrocarbon (PAH) with two fused benzene rings. Under thermal cracking conditions, typically around 500-800ºC in an inert atmosphere can undergo ring opening, fragmentation and rearrangement reactions Jahirul (2012). The process begins primarily with thermal cracking (R1), where $C_{10}H_8$ is broken down into smaller hydrocarbon fragments (C_xH_y) and non-hydrocarbon species such as CO, CO_2, H_2, CH_4, H_2O and carbon species.

Specific cracking includes fragmentations of naphthalene into benzene (C_6H_6) and acetylene (C_2H_2) (R2), phenyl-acetylene (C_8H_6) and ethylene (C_2H_4) (R3), heptendin (C_7H_6) and propane (C_3H_6) (R4). Then, benzyne (C_6H_4) and butene (C_4H_8) (R5) are the possible intermediate cracking of $C_{10}H_8$ that form aromatic and aliphatic fragments.

At higher temperatures, dehydrogenation (R6) possibly can occur, leading to H_2 formation through the loss of H_2 atoms from the aromatic ring system. Then, polymerization or coking (R7) may take place, where $C_{10}H_8$ undergoes condensation and polymerization into solid carbon (coke), releasing additional H_2. Then for hydrogenation path R8, R9 and R10 cracked light olefins ethylene (C_2H_4), propene (C_3H_6) and butene (C_4H_8) to form ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}).

Then, gas-phase reactions involving carbon (C), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2) and steam. The water-gas shift reaction (WGSR) (R11, R13) will react with C and H_2O to form CO and H_2 followed by CO and H_2O to form CO_2 and H_2. In parallel, steam reforming of methane (R12) significantly boosts H_2 production by reacting CH_4 and steam then forming CO_2 and H_2. Then for reactions R14 and R15 at certain conditions where CO or CO_2 reacts with H_2 to regenerate CH_4 and H_2O.

Table 1: Possible reaction of model compound $C_{10}H_8$ under pyrolysis reaction

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	$C_{10}H_8 \rightarrow C_6H_6 + 2C_2H_2$
R3	Thermal cracking	$C_{10}H_8 \rightarrow C_8H_6 + C_2H_4$
R4	Intermediate cracking	$C_{10}H_8 \rightarrow C_7H_6 + C_3H_6$
R5	Intermediate cracking	$C_{10}H_8 \rightarrow C_6H_4 + C_4H_8$
R6	Dehydrogenation	$C_{10}H_8 \rightarrow C_{10}H_6 + H_2 / 2H\cdot \rightarrow H_2$
R7	Polymerization	$C_{10}H_8 \rightarrow 10C$ (solid) + 4 H_2
R8	Hydrogenation	$C_2H_4 + H_2 \rightarrow C_2H_6$
R9	Hydrogenation	$C_3H_6 + H_2 \rightarrow C_3H_8$
R10	Hydrogenation	$C_4H_8 + H_2 \rightarrow C_4H_{10}$
R11	Water gas shift reaction (WGSR)	$C + H_2O \leftrightarrow CO + H_2$
R12	Steam reforming	$CH_4 + H_2O \leftrightarrow CO_2 + 3\ H_2$
R13	Water gas shift reaction (WGSR)	$CO + H_2O \leftrightarrow CO_2 + H_2$
R14	Methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$
R15	Methanation	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$

3.2 Effect of temperature and pressure on H_2 generation

During pyrolysis of $C_{10}H_8$, a variety of thermal reactions may occur depending on temperature, residence time and the presence of radical intermediates generated from FOBS itself during reaction. As previously discussed, several reactions are involved and contribute to producing gas products such as H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, C_4H_8, and C_4H_{10}. In this thermodynamic study, the effect of temperature and pressure was focused on as both parameters significantly influence the energy demand and distribution of pyrolysis products. Figure 2 illustrates the equilibrium composition of gas products produced at a range of temperatures, 273 – 1,273 K and pressures at a range of 1 - 50 bar.

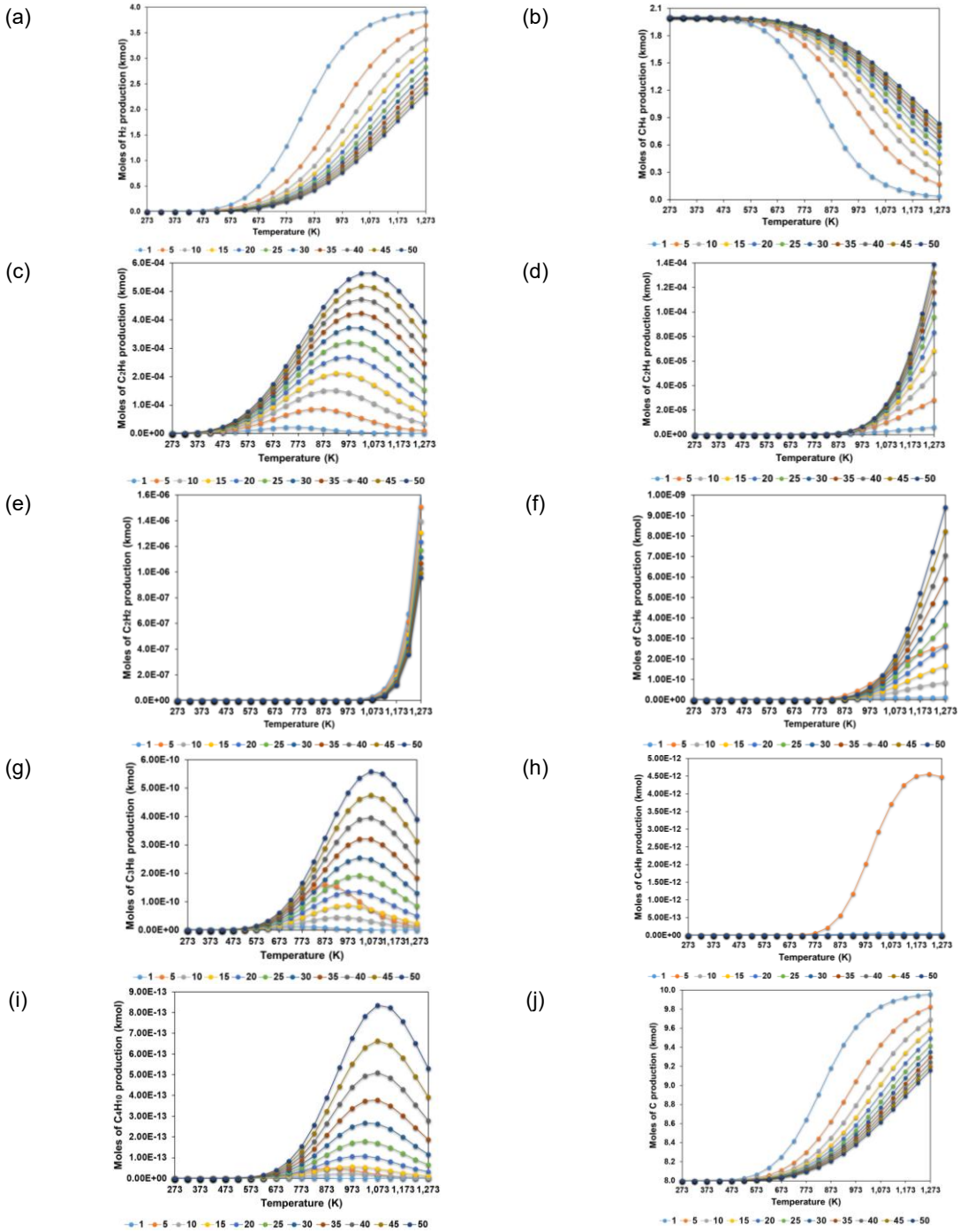

Figure 2: Product produced at temperature 273-1,273 K and pressure 1-50 bar; (a) H_2, (b) CH_4, (c) C_2H_6, (d) C_2H_4, (e) C_2H_2, (f) C_3H_6, (g) C_3H_8, (h) C_4H_8, (i) C_4H_{10} and (j) C

Figure 2a the amount of H_2 produced increased exponentially with rising temperature, particularly beyond 673 K. However, at low pressure, H_2 reached nearly 4 kmol at 1,273 K, while at higher pressure (50 bar), H_2 production is significantly lower, peaking at around 2.3 kmol. This result is parallel with endothermic terms, which favor the formation of lighter gases like H_2 at higher temperature and lower pressure. For CH_4 production in Figure 2b, a descending trend was noticed as temperature increased. The formation of CH_4 can be seen as more favorable at temperatures 273 - 573 K under higher pressure. Temperature beyond 673 K leads to CH_4 formation and nearly disappears at higher temperatures. The decline of CH_4 was in contrast with the H_2 formation, which increased with higher temperature. This might support the possible reaction R12 in Table 1, where CH_4 undergoes steam reforming at high temperature and contributes towards the increase of H_2

generation. This observation aligns with reported trends in the literature, which show that as CH_4 levels decrease, H_2 production tends to increase (Teo et al., 2021b).

Figure 2c depicts the formation of C_2H_6, which peaked highly around 673 - 1,073 K before declining. The formation of C_2H_6 is more favorable at higher pressure. The formation of C_2H_6 was supported by the hydrogenation of C_2H_4 in R8, but under extreme temperatures, C_2H_6 is thermally cracked, and the formation decreased. This kind of breakdown is common during pyrolysis, especially when saturated hydrocarbons become unstable and start forming smaller or unsaturated compounds (Wang et al., 2017).

Figure 2d, 2e and 2f, the production of C_2H_4, C_2H_2 and C_3H_6 is significantly influenced by both temperature and pressure. C_2H_4 begins to rise sharply at a temperature above 873 K and continues to increase with higher temperature and higher pressure. For C_2H_2, minimal production is seen until the temperature exceeds 1,073 K the formation starts peaking. In terms of pressure, it is seen that C_2H_2 was less sensitive towards pressure changes, as overlapping curves across different pressures are illustrated in the figure. These results proved that C_2H_2 formed only thermally, as in R2. While C_3H_6, an increase in trends can be seen as temperature beyond 973 K. C_3H_6 species are seen to be more sensitive to pressure, as higher pressure leads to an increase in the yield. While increasing temperature and pressure promote the formation of C_2H_4 and C_3H_6, their overall concentrations remain relatively low. This is primarily due to competing hydrogenation reactions, such as R8 and R9, where these unsaturated hydrocarbons are further converted into saturated products like C_2H_6 and C_3H_8.

Figure 2g, 2h, and 2i show the production of C_3H_8, C_4H_8 and C_4H_{10}, respectively. For all three products, temperature clearly has a strong effect on their formation, with noticeable increases starting above 673 K. The production of C_3H_8 seems to be supported by the hydrogenation of C_3H_6, which increases alongside H_2 generation. However, its production drops off at 1,173 K, likely due to a decrease in available C_3H_6 at that point. C_4H_8 shows a different behavior where it only forms in significant amounts at 5 bar pressure, which could be due to its formation relying on a specific reaction pathway. Table 1 indicates that C_4H_8 is only produced during the intermediate cracking reaction (R5). As for C_4H_{10}, its production is highest in the 973 - 1,173 K range, which suggests it forms mainly through thermal cracking and hydrogenation reactions, possibly through R1 and R10 pathways.

Then, for Figure 2j the formation of solid carbon (C) is observed to increase progressively with temperature**,** particularly beyond 573 K. However, the extent of carbon formation can be effectively suppressed by applying higher pressures, which shift the equilibrium and reduce carbon yield. At 1,273 K and 1 bar, carbon production reaches a maximum of approximately 9.99 kmol, which is notably higher than the H_2 yield under the same conditions, around 4.0 kmol**.** This highlights that while elevated temperatures promote both H_2 and C formation**,** the H_2:C molar ratio is approximately 1:2.5. This indicates that despite the increase in H_2 production, a significant portion of the feed is converted into carbonaceous by-products, thus limiting the energy efficiency of the process in terms of useful H_2 output.

3.3 Limitations of the thermodynamic study

The thermodynamic study in this work provides the behavior of FOBS under pyrolysis conditions, particularly concerning H_2 generation. However, there are several limitations inherent to this approach that should be highlighted. Firstly, the simulation assumes $C_{10}H_8$ as a single model compound to represent the complex chemical nature of FOBS. While naphthalene is an appropriate choice due to its aromatic structure and thermal stability, it does not fully capture the diverse range of hydrocarbons, heteroatoms, and heavier molecular species typically present in real FOBS. As a result, the thermodynamic predictions may not reflect the actual product distribution, reactivity, or synergetic interactions that occur during the pyrolysis of a multicomponent feedstock.

Secondly, the study reveals that high temperatures are essential to initiate and sustain pyrolytic reactions in FOBS, as no external reactant or catalyst was introduced to lower the energy barrier. This indicates that thermal cracking is the primary mechanism at play, requiring significant energy input. The importance of temperature was strongly reflected in the product yield trends, particularly for H_2 and carbon formation. However, real-world pyrolysis systems often involve complex interactions between components, free radicals, and potentially catalytic surfaces that can shift the reaction pathways and reduce the required energy input.

To enhance the accuracy and applicability of future thermodynamic studies, it is recommended to use a mixture of model compounds, each representing different chemical classes found in FOBS, such as aliphatic hydrocarbons, resins, and asphaltenes. This would allow the investigation of interaction effects, such as how one compound might promote or inhibit the decomposition of another, thereby providing a more representative picture of the actual pyrolysis behavior. Additionally, incorporating kinetic considerations and catalytic effects into the analysis would help bridge the gap between theoretical predictions and experimental outcomes. In conclusion, the current thermodynamic model provides a foundational understanding of H_2 production from FOBS, its scope is limited by the use of a single representative compound and the absence of reaction kinetics or multi-component interaction effects.

4. Conclusions

Based on the thermodynamic study using the Gibbs free energy minimization method, naphthalene ($C_{10}H_8$) was employed as a model compound to represent FOBS. The analysis indicates that FOBS has significant potential to generate H_2 through pyrolysis. Temperature was found to be the primary factor influencing the formation of gaseous products, particularly hydrocarbons and H_2, while pressure showed varying effects depending on the specific compounds involved. H_2 production is primarily supported by several reactions within the pyrolysis process, including thermal cracking, dehydrogenation, polymerization, WGSR, and steam reforming. The highest H_2 yield was observed at 1,273 K and 1 bar, reaching approximately 4.0 kmol. This study is limited to equilibrium-based modelling and does not consider kinetic constraints or detailed process engineering considerations related to hydrogen production from FOBS. Nevertheless, the baseline data generated through this thermodynamic analysis can serve as a reference for future experimental validation and more advanced process simulation studies.

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