

Comparative Study of Thermal, Catalyst-Mediated, Biomass-Assisted, and Combined Upgrading Routes for Nigerian Bitumen over a Hierarchical CoMo/ZSM-5 Zeolite Catalyst

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Abstract

Heavy oil and bitumen tend to be thick, dense, and low in API gravity, and those properties make them more expensive to extract, transport, and refine than conventional crude. This study looked at upgrading Nigerian bitumen using four different approaches: thermal cracking on its own, a hierarchical CoMo/ZSM-5 zeolite catalyst, rice husk biomass acting as a hydrogen donor, and a combined catalyst and biomass system. Each run took place in a batch reactor, with temperature raised from 25 to 350°C under an inert nitrogen atmosphere and then held for 3 hours. The upgraded products were checked for viscosity, density, and API gravity, and both the evolved gas stream and the liquid products were analyzed using Gas chromatography mass spectrometry (GCMS) and Fourier transform infrared (FTIR) spectroscopy. Viscosity dropped sharply, from 28,700 mPa s in the raw feed, down to 285.0, 91.0, 84.6, and 38.2 mPa s for the thermal, catalyst, biomass, and combined runs. API gravity rose from 7.0° to 43.2°, 40.2°, 48.5° and 12.9° across those same runs. Methane showed up as the dominant gas in every case, peaking at 57.1% around the 17 min mark in the catalyst only run. GCMS analysis showed that oxygenated alcohols dominated the thermal and catalyst runs, while carboxylic acids and alkanoate esters dominated the biomass runs; FTIR confirmed oxygenated and aliphatic groups throughout all the products. Taken together, the results show rice husk biomass and the CoMo/ZSM-5 catalyst each improve bitumen's flow properties on their own, but combining them led to an unexpected drop in API gravity, a result that calls for closer mechanistic study.

Keywords: Bitumen upgrading; heavy oil; CoMo/ZSM-5 catalyst; rice husk biomass; thermal cracking; API gravity.

1.0 Introduction

Bitumen is a black, hydrogen deficient mixture of hydrocarbons, obtained naturally or as a residue of petroleum distillation. It is characterized by a low Hydrogen to Carbon ratio and by high Carbon residue, asphaltene, heavy metal, Sulfur, and Nitrogen content. Unlike light conventional crude oil, bitumen and other heavy oils require upgrading; the conversion of heavy feedstock into synthetic crude oil with API gravity, viscosity, and heteroatom content approaching those of light crude, before further refining can take place [1]. Interest in upgrading such resources have grown, as conventional oil reserves decline and enhanced recovery of unconventional feedstocks becomes correspondingly more attractive [2].

Compositionally, heavy oil and bitumen are divided into four fractions: saturates, aromatics, resins and asphaltenes, commonly referred to as the SARA fractions. Asphaltenes and resins, which are the heaviest and most polar of the four, are enriched in heteroatoms such as Sulfur, Nitrogen, and Oxygen, together with trace metals such as Nickel and Vanadium, and form aggregated polycyclic structures that are largely responsible for the very high viscosity of the raw feedstock [3], [4]. Upgrading therefore acts principally on this resin and asphaltene fraction, converting its heavy, heteroatom rich molecules into lighter saturate and aromatic species with a higher hydrogen to carbon ratio.

Heavy oils are generally classified according to API gravity, an index proposed by the American Petroleum Institute and based on the relative density of the oil. Definitions of the cut off point vary across the literature and across national standards bodies; the American Petroleum Institute defines heavy oil as having an API gravity of 20° or lower, while other classification systems place the boundary as high as 22.3° [5]. Oils falling in the 31 to 45° API range are generally regarded as light oil.

Nigeria holds an estimated 38 billion barrels of bitumen and extra heavy oil in place, ranking sixth among countries with the largest such reserves, a quantity that is nonetheless far smaller than the reserves reported for Canada and Venezuela [6]. As conventional oil reserves decline worldwide, unconventional resources of this kind are attracting renewed attention, which makes efficient and low-cost upgrading routes for Nigerian bitumen an important research need.

Bitumen and heavy oil are upgraded either by carbon rejection processes, such as thermal cracking, which are economical but yield a lower quality product, or by Hydrogen addition processes, such as hydrocracking, which

improve product quality at the expense of a high-pressure hydrogen atmosphere [7]–[9]. Both routes have been demonstrated at a range of scales, from horizontal well downhole catalytic upgrading [10] to two stage hydrocracking of petroleum residue [11] and additive based processes for reducing the viscosity of heavy hydrocarbon oils directly [12]; regardless of the specific route chosen, the general processing guideline is to maximize liquid yield by minimizing coke and gas formation [13]. Zeolite catalysts, including the ZSM-5 family, are widely applied in petroleum cracking because of their crystalline microporous structure, high surface area, and shape selective adsorption behaviour, and hierarchical CoMo/ZSM-5 formulations have been reported to promote both cracking and heteroatom removal reactions in heavy feedstocks. Biomass derived hydrogen donors are also of interest because they can supply Hydrogen in situ during cracking, potentially reducing coke formation while improving the saturation of the cracked product, and recent work confirms that biomass hydrogen donors remain effective for heavy feedstock upgrading even though their donating capacity is generally weaker than that of conventional donors such as tetralin [14]. ZSM-5 based catalysts continue to attract attention for upgrading biomass derived and petroleum feedstocks alike, although a recurring limitation reported across recent studies is progressive deactivation by coke deposition within the zeolite micropores during extended time on stream [15]. More recent work reinforces this gap: hierarchical, metal-modified ZSM-5 catalysts have continued to show strong activity for upgrading heavy and medium crude feedstocks [16], and a tri-metal (Mo/Co/Ni) ZSM-5 system evaluated under hydrothermal conditions has recently been shown to combine cracking with in-situ hydrogenation of the resulting radicals [17], while catalytic and non-catalytic routes to in-situ hydrogen generation from heavy oil remain an active area of review [18]; none of these very recent studies, however, directly compares thermal, catalytic and biomass-assisted routes for the same Nigerian bitumen feedstock under identical conditions, which is the gap the present study addresses.

The chemistry of catalytic cracking over zeolites proceeds mainly through carbonium ion intermediates and beta scission at the Bronsted acid sites of the catalyst, with carbonium ions generated by protolytic cracking of paraffins, hydride abstraction, or protonation of olefins at those acid sites, following an initiation, propagation and termination sequence broadly analogous to thermal cracking [19], [20]. This acid catalyzed pathway favours cleavage at C-C, C-S and C-N bonds in a pattern distinct from purely thermal, radical driven cracking [7], which provides a basis for expecting that thermal and catalytic treatment of the same bitumen feedstock can yield upgraded products with different hydrocarbon and heteroatom distributions even where overall conversion is similar.

Rice husk, the biomass hydrogen donor evaluated in this study, is composed of 75 to 90% organic matter, mainly cellulose and lignin, together with a substantial mineral fraction of silica, alkalis and trace elements, with typical elemental content of around 35% Carbon, 4 to 5% Hydrogen, 31 to 37% Oxygen and 17 to 25% Silica, though the exact composition varies with rice variety, soil chemistry and growing conditions [21], [22]. This relatively high Hydrogen and organic content, combined with its wide availability as an agricultural residue in rice producing regions such as Nigeria, makes rice husk a plausible low-cost hydrogen donor candidate for heavy oil upgrading, in addition to its established uses in construction, waste water treatment and heavy metal removal [23], [24].

Despite this interest, there remains limited experimental data comparing thermal cracking, catalytic cracking, and biomass assisted cracking of Nigerian bitumen under identical reactor conditions, and even less data on how these three routes interact when combined. This study therefore investigated the thermal, catalytic, and biomass assisted upgrading of Nigerian bitumen, individually and in combination, over a hierarchical CoMo/ZSM-5 catalyst using rice husk as the biomass hydrogen donor. The specific objectives were to quantify the effect of each treatment on the viscosity, density, and API gravity of the upgraded product, to characterize the evolved gas composition with time on stream, and to examine the chemical composition of the liquid products by GCMS and FTIR.

2.0 Materials and Methods/Methodology

2.1 Materials

Raw Nigerian bitumen was used as the primary feedstock. The hierarchical CoMo/ZSM-5 zeolite catalyst (cobalt-molybdenum supported on Zeolite Sacony Mobil 5) and rice husk biomass were used as upgrading additives, with rice husk selected as an inexpensive, locally available Hydrogen donor. Kerosene and acetone were used as cleaning solvents for the reactor system, and Nitrogen gas was used to purge the reactor to an inert atmosphere before each run. The bitumen used was drawn from the same Agbabu deposit source, Ondo State, Nigeria, as the bitumen characterised and used by Oseni *et al.* [28]. Detailed supplier/batch records for the CoMo/ZSM-5 catalyst and for the rice husk biomass were not retained beyond their description here.

2.2 Equipment

The upgrading reactions were carried out in a laboratory scale batch reactor. Supporting equipment included a weighing balance for feed and additive preparation, a gas analyzer for online monitoring of the evolved gas

stream, a viscometer and a density meter for physical property measurement, together with Fourier transform infrared and gas chromatography mass spectrometry instrumentation for product characterization. Feed and additive masses were recorded on a Mettler Toledo analytical balance, and viscosity was measured with an NDJ-8S digital rotational viscometer. FTIR analysis was carried out on a Shimadzu FTIR-8400S spectrometer, and GCMS analysis on an Agilent 7000D instrument.

2.3 Reactor loading and additive proportions

For each run, 80 g of sample was used. The corresponding feed masses for each run were as follows: for the thermal cracking run, 80.0 g of raw bitumen was charged in the absence of catalyst or biomass. For the bitumen and biomass run, 79.0 g of bitumen was charged with 1.0 g of rice husk biomass, equivalent to a biomass loading of 1.25 wt% of the feed. For the bitumen and catalyst run, 78.88 g of raw bitumen was charged with 1.12 g of CoMo/ZSM-5 catalyst, equivalent to a catalyst loading of 1.40 wt% of the feed.

2.4 Experimental procedure

The batch reactor was first cleaned with kerosene (solvent) before each run, to remove any residue from the previous run. The weighed feed – and, where applicable, catalyst and/or biomass – was charged into the reactor first; Nitrogen gas was then supplied to the loaded reactor for five minutes to purge Oxygen and establish an inert atmosphere before heating began. The charged reactor was heated from an initial temperature of 25°C to a final temperature of 350°C, and held at temperature for a total reaction time of 3 hours. After each run, the gas and liquid products were separated, and the liquid product was recovered for physical property measurement and spectroscopic characterization.

2.5 Analytical methods

Viscosity and density of the raw bitumen and of each upgraded liquid product were measured using a viscometer and a density meter, respectively. Because the raw bitumen feed was too viscous to measure reliably at ambient temperature, its viscosity and density were determined at 66°C, while all upgraded products were measured at the standard reference conditions of 25°C (viscosity) and 15.5°C (density); API gravity was then calculated from the measured density in the standard manner. The composition of the evolved gas stream (CO, CO₂, CH₄ and H₂) was monitored online with the gas analyzer at 1-minute intervals, from the first minute of time on stream up to approximately the 20th–21st minute of each run (the full minute-by-minute record for every run is given in the raw data tables); logging ended at that point while the reactor continued to react, undisturbed, for the remainder of the 3 h holding period. The liquid product was recovered and analyzed only at the end of the full 3 h run. The liquid product from each run was further analyzed by gas chromatography mass spectrometry to identify the relative abundance of individual compounds, and by Fourier transform infrared spectroscopy to identify the functional groups present. The CoMo/ZSM-5 catalyst itself was not independently characterised in this study; this is acknowledged as a limitation, and catalyst characterisation is identified as a priority for future work in the Conclusion.

3.0 Results and Discussion

3.1 Effect of upgrading route on physical properties

Table 1 reports the percentage viscosity reduction and the change in API gravity for each upgraded product relative to the raw bitumen feed; while the corresponding absolute viscosity, density and API gravity values are presented graphically in Figure 1.

Table 1: Percentage viscosity reduction and change in API gravity for the four upgraded products relative to the raw bitumen feed

S/N	Assay	Viscosity reduction (%)	ΔAPI (°)	Dominant reaction pathway
1	Raw bitumen (feed)	-	-	– (N/A)
2	Thermal cracking (TB)	99.01	+36.2	Thermal (radical) C–C scission / beta-scission cracking [7]
3	Bitumen / Catalyst (BC)	99.68	+33.2	Acid-catalyzed carbonium-ion cracking at Bronsted sites (beta-scission) [19, 20]
4	Bitumen / Biomass (BB)	99.71	+41.5	Hydrogen-donation from biomass; radical stabilization, less C–C scission to gas [14]
5	Bitumen / Catalyst / Biomass (BCB)	99.87	+5.9	Competing radical/ionic cracking with hydrogen-donor interference – extensive ring opening / heteroatom-rich fragment formation [25, 17].

Thermal cracking alone reduced viscosity from 28700 to 285.0 mPa s, a reduction of 99.0%, and increased API gravity by 36.2°, from 7.0 to 43.2°. The catalyst only run produced a slightly larger viscosity reduction (99.7%, to 91.0 mPa s, with an API gravity of 40.2°), an increase of 33.2°. The biomass only run gave a comparable viscosity reduction (99.7%), the lowest density of the four products (0.786 kg/L, a 21.4% reduction from the raw feed), and the largest API gravity gain recorded in this study, an increase of 41.5° to 48.5°, indicating a product enriched in shorter chain, more paraffinic hydrocarbons. All three single treatments therefore produced upgraded oil within the light oil classification range (31 to 45° API) and reduced viscosity by more than 99% relative to the raw feed, comfortably below the approximately 343 mPa s (350 cSt) benchmark typically specified for pipeline transportable synthetic bitumen.

The combined catalyst and biomass run behaved differently. It gave the largest viscosity reduction of all four products, 99.9%, to 38.2 mPa s, but its API gravity increased by only 5.9°, to 12.9°, and its density fell by only 2.0%, remaining close to that of the raw feed. This pattern shows that the combined system was the most effective of the four routes at breaking down the large, viscosity controlling molecules in bitumen, yet was the least effective at raising API gravity or lowering density, the two properties that most directly reflect the degree of conversion to lighter, more paraffinic hydrocarbons. Viscosity reduction and API gravity gain are therefore not simply proportional across these four routes, which suggests that the combined catalyst and biomass system favours reaction pathways, such as extensive ring opening or heteroatom rich fragment formation, that lower viscosity without proportionally increasing the Hydrogen to Carbon ratio of the bulk product. Upgrading of this kind proceeds through competing radical and ionic chain reactions, in which olefin intermediates can either propagate toward lighter, more saturated liquid products or condense toward heavier coke precursor material depending on the local availability of hydrogen and active cracking sites [25]; on this basis, the catalyst and the biomass may compete for, or interfere with, the specific reaction pathways that individually raise API gravity when each additive is present alone. This antagonistic interaction between the catalyst and the biomass hydrogen donor was not anticipated from the single treatment results; thus, it represents a specific and testable direction for follow up kinetic and catalytic characterization work, for example by varying the catalyst to biomass ratio and tracking API gravity, density and simulated distillation curves, as a function of that ratio. In the absence of direct characterisation data for the present CoMo/ZSM-5 sample (see Section 2.5), this explanation should be read as a working hypothesis rather than a demonstrated mechanism; the acid-site density, pore hierarchy and metal dispersion of the catalyst would need to be measured and compared between the catalyst-only and catalyst-plus-biomass runs to confirm whether biomass-derived species are competing for, or blocking, the same Bronsted-acid sites responsible for the API gravity gain observed in the catalyst-only run.

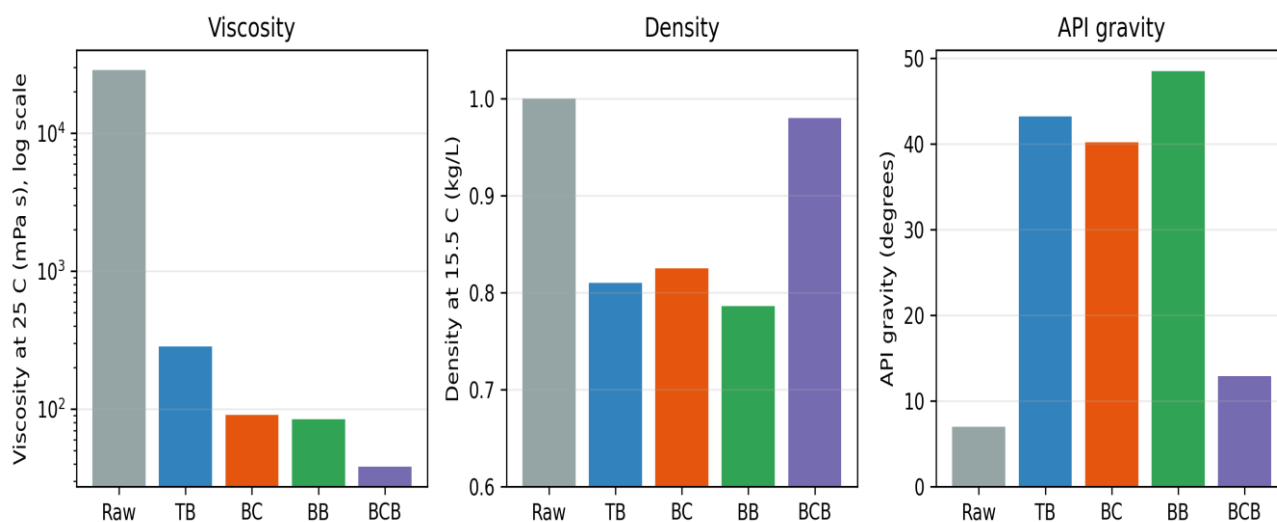


Figure 1: Effect of thermal, catalytic and biomass-assisted upgrading on the viscosity, density and API gravity of bitumen. Viscosity is shown on a logarithmic scale. TB: thermal cracking; BC: bitumen/catalyst; BB: bitumen/biomass; BCB: bitumen/catalyst/biomass

3.2 Gas evolution profiles

Figure 2 presents the evolved gas composition (CO, CO₂, CH₄ and H₂) as a function of time on stream for each of the four runs, based on continuous gas analyzer measurements over 20 to 21 min.

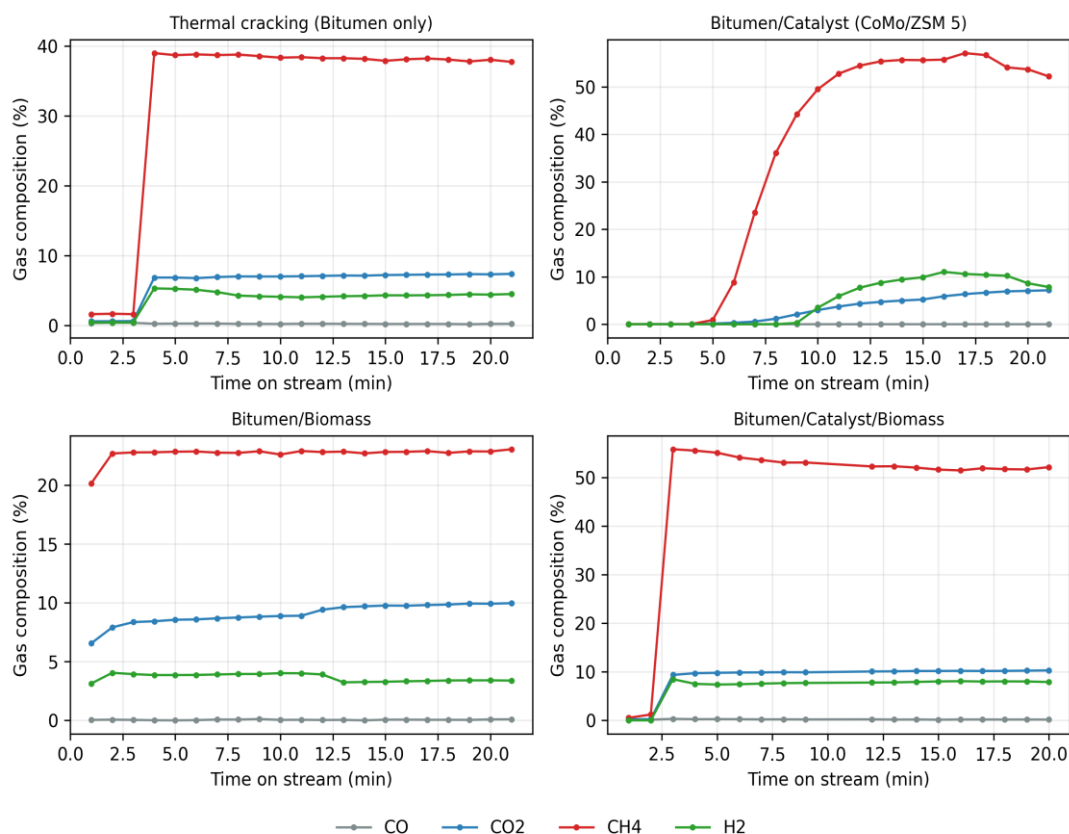


Figure 2: Gas composition against time on stream for the thermal cracking, bitumen/catalyst, bitumen/biomass and bitumen/catalyst/biomass runs

Figure 2 shows that methane was the dominant gas species in all four runs. In the thermal cracking run, methane rose sharply after about three minutes to a plateau near 38 to 39%, while Hydrogen and Carbon dioxide remained comparatively minor. The bitumen/catalyst run showed the most pronounced methane evolution of any run, rising steadily from a negligible level to a peak of 57.1% at 17 min, accompanied by a Hydrogen peak of 11.0% at 16 min, before both gases declined slightly toward the end of the run. The bitumen/biomass run showed the flattest, most stable profile, with methane remaining close to 23% throughout, and Hydrogen close to 3.5 to 4.0%, a level distinctly lower than in the catalyst run. The combined catalyst and biomass run rose very rapidly, reaching a methane peak of 55.8% within three minutes before settling to a plateau near 52%.

To compare the four runs on a common basis, Table 2 reports the mean gas composition over the last five recorded points of each run, representing the approximate steady state condition reached toward the end of the three-hour reaction period.

Table 2: Mean steady state gas composition

Run	CO (%)	CO ₂ (%)	CH ₄ (%)	H ₂ (%)
TB (thermal only)	0.23	7.34	37.97	4.43
BC (catalyst)	0.00	6.82	54.75	9.53
BB (biomass)	0.06	9.89	22.87	3.38
BCB (catalyst + biomass)	0.17	10.21	51.76	7.99

Table 2 shows that on the steady state basis, the bitumen/catalyst run gave the highest mean methane content, 54.8%, followed closely by the combined bitumen/catalyst/biomass run at 51.8%, while the thermal only and bitumen/biomass runs gave substantially lower mean methane contents of 38.0 and 22.9%, respectively. Hydrogen followed the same ranking, with the bitumen/catalyst run again highest at 9.5%. Carbon monoxide remained low, at or below 0.23% on average in every run, indicating that decarbonylation was a minor pathway relative to methane forming cracking reactions across all four routes.

The consistently lower methane and Hydrogen content of the bitumen/biomass run relative to both catalyst containing runs, is consistent with the proposed role of rice husk as a hydrogen donor; by supplying Hydrogen to stabilize cracked radicals in situ, biomass appears to favour retention of Carbon and Hydrogen within the liquid product rather than their loss as light gas, which is also consistent with the higher API gravity and lower density observed for the bitumen/biomass run in Section 3.1. The much faster onset and higher steady state plateau of

methane evolution in both catalyst containing runs confirms the strong cracking activity of the CoMo/ZSM-5 catalyst relative to thermal cracking alone, consistent with the acid catalyzed carbonium ion pathway described in Section 1, in which methane and other light alkanes form directly from C-C bond scission at Bronsted acid sites during protolytic cracking [19]; notably, the combined bitumen/catalyst/ biomass run reached a methane level almost as high as the bitumen/catalyst run despite the presence of biomass, indicating that once the catalyst is present, its cracking activity dominates the gas evolution behaviour even when a Hydrogen donor is co fed, a pattern consistent with the limited API gravity gain already noted for this run in Section 3.1. This is broadly consistent with the mechanism proposed by [17] for a comparable hierarchical, multi-metal ZSM-5 system, in which strong Bronsted-acid-site cracking activity dominates the light-gas-forming pathway once a sufficiently active catalyst is present, even when a hydrogen donor is co-fed; a direct test of this explanation for the present catalyst would require the acid-site density and surface area data noted as outstanding in Section 2.5 above.

3.3 GCMS compositional analysis

GCMS analysis of the liquid products revealed a clear shift in dominant compound class between the catalyst dominated runs and the biomass containing runs, summarized in Table 3.

Table 3: Summary of the dominant compound class identified by GCMS in each run

Run	Dominant compound class (GCMS)	Representative compound	Area (%)
TB (thermal only)	Oxygenated alcohol	2-Propanol, 1,1,1-trichloro-2-methyl	11.47
BC (catalyst)	Oxygenated alcohol / alkane	2-Propanol, 1,1,1-trichloro-2-methyl	11.50
BB (biomass)	Carboxylic ester (alkanoate)	9-Octadecenoic acid (Z)-, methyl ester	45.83
BCB (catalyst + biomass)	Carboxylic ester (alkanoate)	9-Octadecenoic acid, methyl ester	25.11

For the thermal cracking and bitumen/catalyst runs, the most abundant identified species were oxygenated alcohols, exemplified by 2-propanol, 1,1,1-trichloro-2-methyl. For the bitumen/biomass and bitumen/catalyst/biomass runs, the dominant oxygenated species shifted to carboxylic acids and their methyl esters (alkanoates), exemplified by 9-octadecenoic acid and its methyl ester, together with hexadecanoic acid methyl ester and heptadecanoic acid methyl ester. This shift in oxygenate class between the biomass free and biomass containing runs is consistent with the biomass itself contributing fatty acid and ester type oxygenated fragments to the liquid product during co processing, in addition to its role as a hydrogen donor, and broadly mirrors the saturate, aromatic, resin and asphaltene (SARA) framework used to classify heavy oil composition more generally, in which the resin and asphaltene fractions carry most of the heteroatom and oxygenated functionality of the parent bitumen [3], [4].

3.4 FTIR analysis

Figure 3 shows the FTIR spectra recorded for the thermal cracking, bitumen/catalyst, bitumen/biomass and bitumen/catalyst/biomass liquid products, and Table 4 summarizes the band assignments used to interpret them.

Table 4: FTIR band assignments used to interpret the liquid product spectra

Wavenumber (cm ⁻¹)	Assignment	Functional group/class
2500 to 3000	O-H and CH ₂ stretching	Oxygenated (alcohol) and aliphatic (alkane) groups
1000 to 1500	C=O stretching	Oxygenated (carbonyl compound)
1000 to 1500	CH ₂ bending	Aliphatic (alkane)

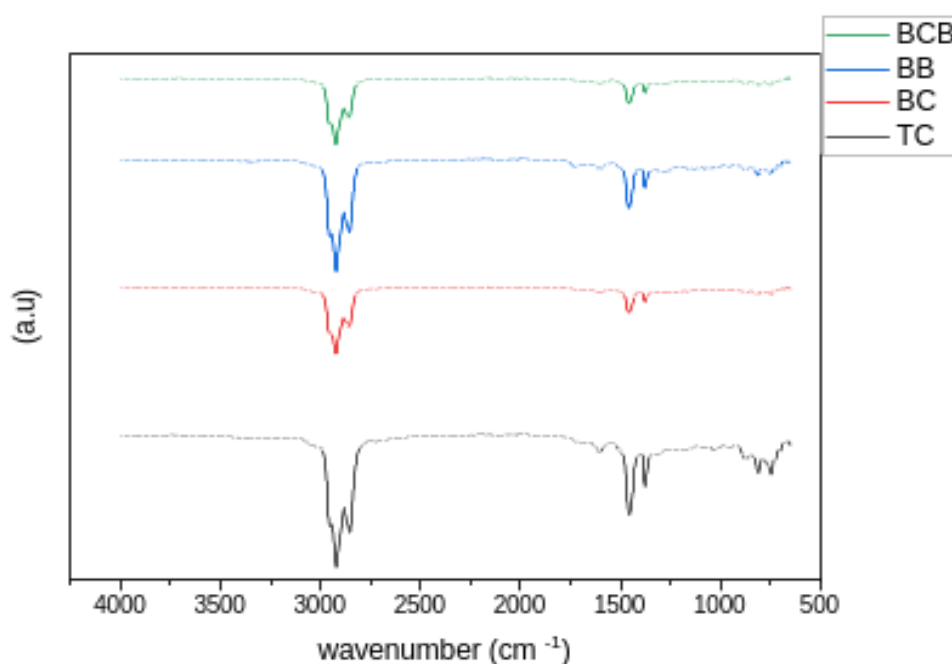


Figure 3: FTIR spectra of the thermal cracking (TC), bitumen/catalyst (BC), bitumen/biomass (BB), and bitumen/catalyst/biomass (BCB) liquid products

FTIR spectra of the liquid products from the thermal cracking, bitumen/biomass and bitumen/catalyst/biomass runs showed absorption bands consistent with oxygenated and aliphatic functional groups. Bands between 2500 and 3000 cm^{-1} , assigned to O-H and CH_2 stretching vibrations, were present in all spectra, together with bands between 1000 and 1500 cm^{-1} , assigned to carbonyl ($\text{C}=\text{O}$) stretching, confirming the presence of oxygenated groups, and to CH_2 bending, confirming the presence of aliphatic alkane groups. These assignments are consistent with functional group patterns reported elsewhere for bituminous binders [26].

3.5 Summary of findings

The physical property, gas evolution and compositional results indicate that both the CoMo/ZSM-5 catalyst and rice husk biomass are independently effective at improving the flow properties of Nigerian bitumen, but that they act through distinguishable chemical routes; while the catalyst promotes extensive cracking to light gas and short chain oxygenates, the biomass moderates gas evolution and shifts the liquid product toward fatty acid and ester type oxygenates while still achieving a favourable API gravity. Their combined use gave the lowest viscosity of all treatments but did not produce the expected additive improvement in API gravity. More broadly, the results support the view that upgrading routes should consider liquid yield, gas and coke formation, and heteroatom removal, rather than only viscosity or API gravity gain in isolation [13], [27], since the present dataset shows that the route that gave the largest viscosity reduction was not the same route that gave the largest gain in API gravity. This viscosity performance compares favourably with recent hierarchical, metal-modified ZSM-5 systems reported for heavy oil upgrading: for example, [17] reported a 75.7% viscosity reduction for a tri-metal Mo/Co/Ni-ZSM-5 catalyst under aquathermolysis conditions, well below the 99.68% and 99.87% reductions achieved here for the catalyst-only and combined catalyst/biomass routes respectively, although the two studies differ in feedstock, catalyst formulation and operating atmosphere, so this comparison should be treated as indicative rather than a controlled benchmark.

4.0 Conclusion

Thermal cracking, catalytic upgrading over a hierarchical CoMo/ZSM-5 catalyst, and biomass assisted upgrading using rice husk as a Hydrogen donor, were each effective at improving the flow properties of Nigerian bitumen, reducing viscosity by more than 90% and raising API gravity into the light oil range. Methane was the principal evolved gas across all runs, reaching its highest level in the catalyst only run, while the biomass containing runs showed comparatively suppressed gas evolution and produced the highest API gravity recorded in this study. GCMS analysis showed that biomass addition shifted the dominant oxygenated species in the liquid product from alcohols toward carboxylic acids and their esters, and FTIR confirmed oxygenated and aliphatic functional groups in all upgraded products. Combining the catalyst and biomass gave the greatest viscosity reduction but an unexpectedly modest gain in API gravity, indicating an interaction between the two additives that warrants further mechanistic investigation. These findings support the use of rice husk biomass, an inexpensive and widely available

agricultural residue, as a practical hydrogen donor for the upgrading of Nigerian heavy oil and bitumen, and identifies catalyst to biomass ratio optimization as a priority for future work aimed at maximizing both flow property improvement and API gravity gain simultaneously. Independent characterisation of the CoMo/ZSM-5 catalyst (BET surface area, XRD, SEM/TEM, and NH₃-TPD acidity), which was not performed in this study, is identified as a further priority for future work to support direct mechanistic interpretation of the results reported here.

References

- [1] A. J. Carrillo and M. L. Corredor, "Upgrading of heavy crude oils: Castilla," *Fuel Process. Technol.*, vol. 109, pp. 156–162, 2013.
- [2] S. Thomas, "Enhanced oil recovery: an overview," *Oil Gas Sci. Technol.*, vol. 68, no. 1, pp. 9–19, 2008.
- [3] I. A. Wiehe, "A phase separation kinetic model for coke formation," *Ind. Eng. Chem. Res.*, vol. 32, no. 11, pp. 2447–2454, 1993.
- [4] J. H. Pacheco-Sanchez, F. Alvarez-Ramirez, and J. M. Martinez-Magadan, "Morphology of aggregated asphaltene structural model," *Energy Fuels*, vol. 18, pp. 1676–1686, 2004.
- [5] J. G. Speight, *The Chemistry and Technology of Petroleum*, 4th ed. Boca Raton, FL: CRC Press, 2007.
- [6] C. Milos, *Bitumen in Nigeria: Weighing the True Costs of Extraction*. Abuja: Heinrich Boell Foundation Nigeria, 2015.
- [7] P. M. Rahimi and T. Gentzis, "The chemistry of bitumen and heavy oil processing," in *Practical Advances in Petroleum Processing*, vol. 1. New York: Springer, 2006, pp. 149–186.
- [8] J. G. Speight, *Oil Sand and Tar Sand Production Processes*. Oxford: Gulf Professional Publishing, Elsevier, 2013.
- [9] M. R. Gray, *Upgrading Oil Sands Bitumen and Heavy Oil*. Edmonton: Univ. of Alberta Press, 2015.
- [10] M. Greaves, "CAPRI horizontal well reactor for catalytic upgrading of heavy oil," in *Preprints*, Amer. Chem. Soc., Div. Petrol. Chem., 2000.
- [11] C. Guan, Z. Wang, and D. Wehunt, "Upgrading petroleum residue by two stage hydrocracking," *Fuel Process. Technol.*, vol. 85, pp. 165–172, 2003.
- [12] J. P. Diebold, J. W. Scahill, H. L. Chum, R. J. Evans, B. Rejai, R. L. Bain, and R. P. Overend, "Process for reducing the viscosity of heavy hydrocarbon oils," U.S. Patent 5,096,566, 1992.
- [13] T. Kaminski, Q. Sheng, and M. M. Husein, "Hydrocracking of Athabasca vacuum residue using Ni-Mo-supported drill cuttings," *Catalysts*, vol. 9, no. 3, p. 216, 2019.
- [14] G. Deng, X. Tang, J. Li, S. Ling, Z. Yang, D. Qing, and H. Wang, "The application prospect of biomass hydrogen-donors in steam-assisted oil recovery," *Int. J. Hydrogen Energy*, vol. 110, pp. 251–270, 2024.
- [15] I. Kariim, H. Swai, and T. Kivevele, "Bio-oil upgrading over ZSM-5 catalyst: a review of catalyst performance and deactivation," *Int. J. Energy Res.*, vol. 2023, pp. 1–33, 2023.
- [16] J. Zhong, K. Li, J. Lei, J. Lv, J. Liu, F. Subhan, P. Peng, Y. Wang, and Z. Yan, "Preparation and application of hierarchical ZSM-5 based catalysts for upgradation of Saudi Arabia's medium crude oil," *J. Porous Mater.*, vol. 31, no. 2, pp. 463–471, 2024.
- [17] Y. Sun, S. Li, C. Xiao, Q. Liu, D. Wei, and J. Yang, "Improving catalytic aquathermolysis of heavy oil using a tri-metal supported zeolite catalyst," *RSC Adv.*, vol. 16, no. 29, pp. 26609–26622, 2026.
- [18] M. A. Hanfi, O. S. Alade, A. Tanimu, M. Mahmoud, and S. A. Alarifi, "Catalytic and noncatalytic in situ hydrogen production from heavy oil: a review of experimental studies," *ACS Omega*, vol. 9, no. 51, pp. 50118–50133, 2024.
- [19] G. Jian-hong, J. Long, and Y. Xu, "Protolytic cracking in Daqing VGO catalytic cracking process," *J. Fuel Chem. Technol.*, vol. 36, no. 6, pp. 691–695, 2008.
- [20] H. J. Lee, S. Kang, Y. Kim, and S. Park, "New approach for kinetic modelling of catalytic cracking of paraffinic naphtha," *Ind. Eng. Chem. Res.*, vol. 50, pp. 4264–4279, 2011.
- [21] A. S. Muntohar, "Utilization of uncontrolled burnt rice husk ash in soil improvement," *Dimensi Teknik Sipil*, 2002.
- [22] A. Muthadhi, "Rice husk ash: properties and its uses, a review," *IE(I) J.*, vol. 88, 2007.
- [23] E. Munaf and R. Zein, "The use of rice husk for removal of toxic metals from waste water," *Environ. Technol.*, 2010.
- [24] S. Lata and S. R. Samadder, "Removal of heavy metals using rice husk: a review," *Int. J. Environ. Res. Develop.*, 2014.
- [25] M. R. Gray and W. C. McCaffrey, "Role of chain reactions and olefin formation in cracking, hydroconversion and coking of petroleum and bitumen fractions," *Energy Fuels*, vol. 16, pp. 756–766, 2002.
- [26] B. Hofko *et al.*, "FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature," *Mater. Struct.*, vol. 51, no. 2, p. 45, 2018.

- [27] C.-X. Yin and M. R. Gray, "Separation of petroporphyrins from asphaltenes by chemical modification and selective affinity chromatography," *Energy Fuels*, vol. 23, pp. 2600–2605, 2009.
- [28] Y. M. Oseni, U. O. Aroke, and B. Y. Jibril, "Optimised condition catalytic upgrading of Agbabu bitumen in the presence of rice husks," *Path Sci.*, vol. 10, no. 4, pp. 6001–6021, 2024.
- [29] P. O. Nwosibe, A. Y. Atta, S. M. Shuwa, J. M. Sani, and B. Y. Jibril, "Catalytic upgrading of heavy oil using FCC equilibrated catalyst," *Sci. Forum (J. Pure Appl. Sci.)*, vol. 21, pp. 291–296, 2021.