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# Biomass-Derived Hydrogen Donor and Equilibrated Zeolite Assisted Upgrading of Extra Heavy Bitumen: Reactor Response, Viscosity Reduction, and Compositional Shift

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**ABSTRACT**

Nigerian bitumen sourced from Agbabu, Ondo State, is classified as an extra heavy oil, with an API gravity of 8.6° and a viscosity of 32000 mPa s at 40°C, properties that render it unsuitable for pipeline transportation or direct refinery feedstock without prior upgrading. This study evaluated hydrogen addition upgrading of the bitumen using three renewable biomass derived hydrogen donors, glycerol, sawdust, and rice husk (each added at 5 wt% of the bitumen charge, or 5 mL for glycerol), assessed individually and with rice husk further combined with an equilibrated zeolite catalyst (0.4 wt%), benchmarked against pyrolysis alone and catalytic upgrading without a hydrogen donor. Runs were performed in a high pressure batch reactor pressurized with 10 bar nitrogen and heated to 350°C, with pressure and temperature recorded at 10 min intervals. Upgraded liquid products were characterized for viscosity, density, and API gravity, and analyzed by Fourier transform infrared (FTIR) and gas chromatography mass spectrometry (GCMS). Viscosity decreased from 32000 mPa s in the raw feedstock to between 1900 and 2700 mPa s across the upgrading routes, a reduction of 90.6 to 94.1%, while API gravity rose from 8.6° to between 24.3° and 28.9°. The combination of rice husk and catalyst produced the most favorable outcomes, yielding the greatest viscosity reduction and highest API gravity; this ranking was consistent across all routes, with sawdust the least effective additive. Reactor pressure rise, indicative of gas evolution, was likewise greatest for the rice husk and combined runs. These findings establish rice husk as a cost effective, promising renewable hydrogen donor for bitumen upgrading, particularly with zeolite catalysis.

**Keywords:** Bitumen Upgrading; Hydrogen Donor; Biomass; Rice Husk; Zeolite Catalyst; API Gravity

## INTRODUCTION

Bitumen has been used by humans since antiquity, known by different names to the Sumerians, Akkadians and Arabs of Iraq, and used by the Mesopotamians, Egyptians, Babylonians and Assyrians for purposes ranging from attaching arrowheads to shafts, to waterproofing vessels (Bilkadi, 2018). In its modern industrial sense, bitumen is a black, sticky, non-crystalline solid or highly viscous substance composed largely of condensed polycyclic aromatic hydrocarbons, heterocyclic compounds and trace heavy elements, such as Nickel, Vanadium and Sulfur, and it is used mainly for road construction as well as an adhesive, sealant and waterproofing agent (Bejjenki, 2015).

Heavy crude oil is generally defined as a liquid petroleum with an API gravity below 20°, while extra heavy oil is defined by an API gravity below 10° (Milos, 2015). Bitumen, sometimes called sand oil, is a naturally occurring extra heavy oil that requires additional processing to extract, transport and refine relative to lighter conventional oil (Milos, 2015), and it can be classified as either refined bitumen, recovered as a bottom product of conventional crude oil refining, or natural bitumen, which occurs and is mined directly and requires substantially more processing before it can be transported or refined (Bejjenki, 2015). Bitumen is deficient in Hydrogen relative to conventional crude oil, and it is generally classified by its Sulfur, Carbon residue, Nitrogen and metals content, and it is compositionally divided into saturates, aromatics, resins and asphaltenes, with the polar resin and asphaltene fractions responsible for much of its viscoelastic behaviour and its affinity for solid aggregates (Gary, Handwerk, and Kaiser, 2007; Oblad, 1997).

Nigeria holds a large bitumen deposit, estimated at 38 billion barrels, concentrated mainly in the South West of the country, a quantity broadly comparable to the nation's conventional crude oil reserve (Milos, 2015). This resource remains largely untapped, in part because of the technical difficulty of extracting, transporting and refining a feedstock of such high viscosity and low API gravity. Upgrading bitumen into a lighter, more mobile synthetic crude is therefore a prerequisite for its use as a refinery feedstock, and can proceed either by carbon rejection processes, such as solvent deasphalting, visbreaking and coking, which remove carbon rich material from the feed, or by Hydrogen addition processes, in which an external hydrogen source is supplied to saturate the cracked fragments and improve product quality; the choice between these routes is generally guided by the Sulfur, metal and asphaltene content and the API gravity of the specific feedstock (Bannerjee, 2012; Gray, 2015).

Hydrogen addition can be carried out either by supplying Hydrogen gas directly or through a Hydrogen donor compound, whose primary function is to inhibit the condensation reactions that would otherwise reform heavy, coke precursor molecules during cracking. Traditional Hydrogen donors such as tetrahydrofuran and tetrahydronaphthalene are not well suited to commercial scale application, which has motivated interest in renewable alternatives; glycerol, an abundant low value byproduct of

biodiesel production, has been reported as an effective hydrogen donor, and lignocellulosic biomass more broadly, through the thermal decomposition of its cellulose and hemicellulose fractions at 300 to 400°C, yields a range of small, polar organic molecules that may similarly contribute to heavy oil upgrading (Bannerjee, 2012). Renewable biomass materials are attractive as Hydrogen donors for this purpose because they are inexpensive, widely available as agricultural or process residues, and offer a route to reduce reliance on purchased hydrogen gas. Biomass itself is understood as any material currently derived from plants that use sunlight to grow, and, provided it is not consumed faster than it can be regrown, its use as an energy or process resource keeps the surrounding Carbon cycle close to balance (Quaak, Knoef, and Stassen, 1999). Rice husk and sawdust are abundant lignocellulosic residues in Nigeria, while glycerol is a distinct, non lignocellulosic byproduct stream; each has a different Hydrogen, Oxygen and Carbon content and thermal decomposition behaviour that could influence its effectiveness as a Hydrogen donor during bitumen upgrading (Klass, 1998). The mechanisms by which these Hydrogen donors supply reactive Hydrogen to the bitumen matrix differ according to their chemical nature. Lignocellulosic biomass, such as Rice husk and Sawdust, is built largely from cellulose, hemicellulose and lignin; thermal breakdown of these polymers during pyrolysis, generates a spectrum of reactive intermediate species, including light organics and non-condensable gas (largely CO, $CO_2$ and $H_2$) from cellulose and hemicellulose decomposition, and phenolic fragments released as lignin, a three dimensional polymer of propenylphenol and methoxylated propenylphenol units, breaks down (Diebold and Bridgwater, 1997; Behrendt et al., 2008). Several of these intermediates are understood to donate Hydrogen to, or cap, the free radicals generated during bitumen cracking. Glycerol, by contrast, is a small polyol without a lignocellulosic structure; under thermal stress it principally undergoes dehydration to acrolein and related light oxygenates, a donation pathway distinct from the char and tar forming steps characteristic of solid biomass pyrolysis. While for Rice husk, beyond its organic decomposition products, it is also distinguished from Sawdust by a substantially higher mineral ash content, dominated by silica together with alkali and alkaline earth species; mineral matter of this kind has been reported elsewhere to act as an in-situ promoter of tar cracking and gas formation during biomass pyrolysis (Dayton, 2002) Thus, renewable Hydrogen donors of this kind have also begun to attract dedicated attention as a route to in-situ heavy oil upgrading (Deng et al., 2024), reinforcing the rationale for their evaluation here.

This study investigated the upgrading of Nigerian bitumen using three biomass hydrogen donors (glycerol, sawdust and rice husk) individually, and using rice husk in combination with an equilibrated zeolite catalyst, benchmarked against pyrolysis alone, and catalytic upgrading without an added Hydrogen donor. Unlike upgrading studies that report only the final product properties, this study also tracked reactor pressure and temperature throughout each run, which provides a time resolved indicator of when and how vigorously cracking and gas evolution occurred under each treatment. The specific objectives were to characterize the raw bitumen, to quantify the effect of each of the upgrading routes on viscosity, density and API gravity, to compare the reactor pressure and temperature response of the routes, and to characterize the chemical composition of the upgraded liquid products by FTIR and GCMS.

## MATERIALS AND METHODS

### Materials

Raw bitumen was sourced from Agbabu, Ondo State, Nigeria. Sawdust and rice husk, used as biomass Hydrogen donors, were sourced from Samaru and Basawa respectively, both in Zaria, Kaduna State; these two lignocellulosic residues were selected as inexpensive, locally abundant agricultural and forestry byproducts (Demirbas, 2001). Glycerol, the third Hydrogen donor evaluated, was obtained as a laboratory reagent and was included as a representative non lignocellulosic Hydrogen donor of the kind generated as a low value byproduct of biodiesel production (Bannerjee, 2012). An equilibrated zeolite based catalyst (E-Cat) was obtained from the Kaduna Refining and Petrochemical Company (KRPC), Kaduna State. Nitrogen gas was used to pressurize the reactor and establish an inert atmosphere. The E-Cat and the two biomass feedstocks were used as received; no independent physicochemical characterization (e.g., BET surface area, powder XRD or XRF for the catalyst; proximate, ultimate or particle size analysis for the sawdust and rice husk) was performed in this study. However, some characterization (FTIR XRD, and XRF) have been carried out on the catalyst in a previous study (Nwosibe et al., 2021), which has now been referenced in this work

### Equipment

Upgrading reactions were carried out in a high pressure batch Parr reactor. A weighing balance was used for feed and additive preparation, a digital viscometer for viscosity measurement, an FT-IR spectrometer for functional group analysis of the liquid products, and a GC-MS instrument (Varian 3800/4000 GC-MS) for detailed compositional analysis. An oven was used to dry the sawdust and rice husk prior to use.

### Feedstock Characterization

The raw bitumen was characterized for flash point, fire point, penetration, specific gravity, ductility, solubility and softening point, and its viscosity was measured at 40°C. Density and specific gravity of the raw bitumen and of each upgraded liquid product were determined gravimetrically, and API gravity was then calculated from specific gravity using the standard relationship API equals 141.5 divided by specific gravity, minus 131.5.

### Experimental Procedure

Six upgrading runs were carried out. In the pyrolysis only run, 100 g of raw bitumen was charged to the reactor with no catalyst or biomass. In the catalyst only run, 100 g of bitumen was charged together with 0.4 g of the equilibrated zeolite catalyst. In each of the three biomass runs, 100 g of bitumen was charged together with 5 g of sawdust, 5 g of rice husk, or 5 ml of glycerol respectively; the sawdust and rice husk were sieved and oven dried at 100°C for 1 h before use. In a sixth, combined run, 100 g of bitumen was charged together with both 5 g of rice husk and 0.4 g of catalyst, based on the(later) results/finding that rice husk gave the most favourable single donor result. In every run, the sealed reactor was pressurized with 10 bar of Nitrogen. the Nitrogen source was then disconnected, and the reactor was heated to a set point of 350°C; reactor pressure and temperature were logged at 10 min intervals throughout. Each run was allowed to proceed for 1 h once the set point was reached, after which the reactor was cooled to room temperature before the liquid product was recovered for analysis. In the three biomass runs, a stirrer was additionally engaged at 120 rpm; the pyrolysis only and catalyst only runs did not include a stirrer. However, since

heat and mass transfer in this high-viscosity feedstock (32000 mPa s at 40°C) are strongly diffusion-limited; stirring itself, alters thermal conductivity and interfacial contact between cracking fragments, so differences in reactor response between the stirred biomass runs and the unstirred pyrolysis-only and catalyst-only runs reflect the combined effect of the hydrogen donor chemistry and improved heat/mass transfer, and cannot be attributed to the additive alone.

**Analytical Methods**

Viscosity of each liquid product was measured at 40°C using the digital viscometer. FTIR spectra were recorded for each liquid product to identify the functional groups present, using the wavenumber assignments summarized in Table 3. GCMS analysis was carried out on the raw bitumen and on each of the six upgraded products to identify individual compounds and their relative abundance (percentage peak area and percentage weight).

## RESULTS AND DISCUSSION

### Physicochemical Properties of the Raw Bitumen

**Table 1: Physicochemical Properties of the Raw Agbabu Bitumen**

| S/N | Property | Value |
|---|---|---|
| 1 | Flash point | 240°C |
| 2 | Fire point | 260°C |
| 3 | Penetration | 139.3 (units as recorded in source) |
| 4 | Specific gravity | 1.01 |
| 5 | Ductility | 80 cm |
| 6 | Solubility | 80% |
| 7 | Softening point | 41°C |
| 8 | API gravity | 8.6° |
| 9 | Viscosity at 40°C | 32000 mPa s |

The raw bitumen had an API gravity of 8.6°, placing it within the extra heavy oil category (API gravity below 10°), and a viscosity of 32000 mPa s at 40°C, more than an order of magnitude higher than that of a typical light conventional crude. This combination of low API gravity and very high viscosity is consistent with the general behaviour reported for other extra heavy oils (Santos, Loh, Bannwart, and Trevisan, 2014) and confirms that the Agbabu bitumen requires substantial upgrading before it can be considered for pipeline transport or as refinery feedstock.

**Reactor Pressure and Temperature Response**

Figure 1 presents the reactor pressure and temperature recorded at 10 min intervals for each of the six runs.

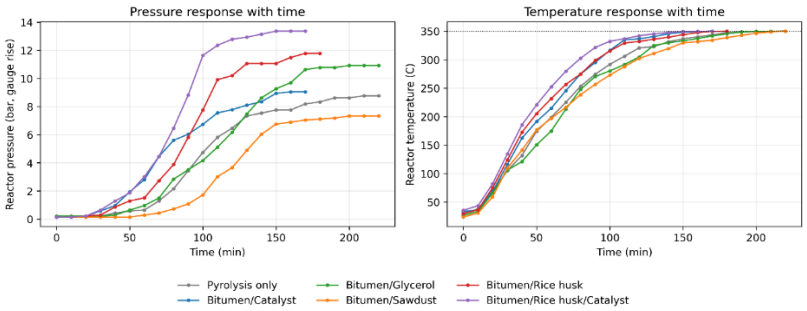



Figure 1: Reactor Pressure (Left) and Temperature (Right) Response with Time for the Six Upgrading Runs

Reactor pressure, which reflects the volume of gas evolved as cracking proceeds, rose most rapidly and reached the highest final value for the combined rice husk and catalyst run (13.4 bar) and the rice husk only run (11.8 bar), followed by the glycerol run (10.9 bar) and the catalyst only run (9.0 bar), with the pyrolysis only run (8.8 bar) and the sawdust run (7.3 bar) showing the lowest final pressures. The sawdust run also showed a distinctly delayed onset, with little pressure rise before about 50 to 60 min, consistent with a slower initiation of cracking reactions relative to the other five routes. This difference is broadly consistent with the compositional and mineral matter differences reported in the literature for rice husk and sawdust as biomass feedstock's. Rice husk carries a substantially higher ash content, on the order of 16 to 18 wt%, than sawdust, whose ash content is typically below 1.5 wt%, while sawdust has both a higher volatile matter content and a higher heating value than rice husk (Blasi, 2009). Mineral matter of the kind concentrated in rice husk ash, largely silica together with alkali and alkaline earth species, has been associated in the biomass pyrolysis literature with catalytic effects on tar cracking and gas formation (Dayton, 2002), which offers a plausible, though not directly confirmed, explanation for why rice husk produced an earlier and larger pressure rise than sawdust despite sawdust's higher intrinsic volatile matter content; this hypothesis was not tested directly in the present study and would require ash resolved kinetic experiments to confirm.

Reactor temperature rose along a broadly similar path for all six runs over the first 100 min, after which the combined rice husk and catalyst, rice husk only, and catalyst only runs reached the 350°C set point soonest, at 170, 180 and 170 min respectively, while the pyrolysis only, glycerol and sawdust runs took longer, all three reaching the set point only at 220 min. The roughly 50 min longer time taken by the sawdust and glycerol runs to reach set point, relative to the unstirred catalyst-only run (170 min), is notable, precisely because sawdust and glycerol were stirred, while catalyst-only was not; and stirring would be expected to shorten, not lengthen,

this interval. The delay is therefore more plausibly explained by an endothermic heat penalty from moisture vaporisation and the early stages of volatile thermal cracking in these feedstocks, which consumes latent heat before the bulk temperature can resume its rise, than by the stirring difference itself. The earlier onset of pressure rise and the shorter time to reach set point temperature in the catalyst containing and rice husk containing runs both point to more active early cracking chemistry in these systems relative to pyrolysis alone, glycerol, or sawdust. Because a magnetic stirrer was engaged only in the three biomass runs (Section 2.4), part of the more rapid response observed for the rice husk and combined runs cannot be attributed to the hydrogen donor alone; improved heat and mass transfer from stirring is a plausible contributing factor that should be isolated in a follow up study using a matched stirring protocol across all six runs.

**Effect of Hydrogen Donor on Viscosity, Density and API Gravity**

Table 2 summarizes the viscosity, specific gravity and API gravity of the raw bitumen and of the six upgraded products, together with the percentage viscosity reduction relative to both the raw feed and the pyrolysis only baseline, and the change in API gravity relative to the raw feed. Figure 2 presents the viscosity and API gravity data graphically.

**Table 2: Viscosity, Specific Gravity and API Gravity of the Raw Bitumen and The Six Upgraded Products, With Percentage Viscosity Reduction and Change in API Gravity**

| Run | Viscosity (mPa s) | Specific gravity | API (°) | Visc. reduction vs raw (%) | Visc. reduction vs pyrolysis (%) | ΔAPI vs raw (°) |
|---|---|---|---|---|---|---|
| Raw bitumen | 32000 | 1.01 | 8.6 | - | - | - |
| Pyrolysis only | 3000 | 0.908 | 24.3 | 90.63 | - | +15.7 |
| Bitumen / Catalyst | 2500 | 0.894 | 26.8 | 92.19 | 16.67 | +18.2 |
| Bitumen / Glycerol | 2650 | 0.897 | 26.2 | 91.72 | 11.67 | +17.6 |
| Bitumen / Sawdust | 2700 | 0.902 | 25.4 | 91.56 | 10.00 | +16.8 |
| Bitumen / Rice husk | 2200 | 0.889 | 27.7 | 93.13 | 26.67 | +19.1 |
| Bitumen / Rice husk / Catalyst | 1900 | 0.882 | 28.9 | 94.06 | 36.67 | +20.3 |

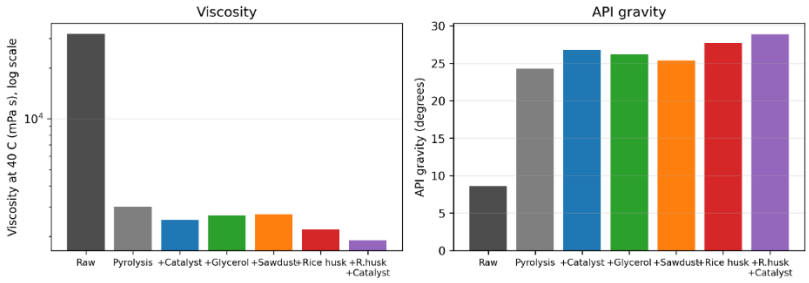



Figure 2: Viscosity (Logarithmic Scale, Left) and API Gravity (Right) of the Raw Bitumen and the Six Upgraded Products

All six upgrading routes reduced viscosity by more than 90% relative to the raw feed and raised API gravity from 8.6° into the 24° to 29° range. Comparing the five additive containing runs against the pyrolysis only baseline, isolates the specific contribution of each additive: sawdust gave the smallest additional benefit (10.0% further viscosity reduction and a 1.1° further API gravity gain relative to pyrolysis alone), glycerol gave a modestly larger benefit (11.7%, 1.9°), the catalyst alone gave a larger benefit still (16.7%, 2.5°), rice husk alone gave a substantially larger benefit (26.7%, 3.4°), and rice husk combined with catalyst gave the largest benefit of all (36.7%, 4.6°).

Notably, this ranking, sawdust, then glycerol, then catalyst alone, then rice husk alone, then rice husk with catalyst, is identical whether the routes are ranked by viscosity reduction or by API gravity gain. This is a different pattern from what is sometimes observed when combining a cracking catalyst with a Hydrogen donor, where the two properties can respond in different directions. In this study, viscosity reduction and API gravity gain moved together and were mutually reinforcing across every route tested, and rice husk combined with catalyst was unambiguously the most effective treatment on both measures. Hydrogen donors of this kind are understood to act primarily by inhibiting the condensation reactions that would otherwise reform heavy, coke precursor molecules during cracking, rather than by promoting cracking directly (Bannerjee, 2012); the results suggest that, in this system, rice husk supplies Hydrogen in a way that is compatible with, rather than competing against, the cracking activity of the zeolite catalyst, so that the two mechanisms reinforce one another instead of trading off.

**FTIR Functional Group Analysis**

Figure 3 shows the FTIR spectra recorded for the raw bitumen and the six upgraded products, and Table 3 summarizes the wavenumber ranges and corresponding functional group and compound class assignments used to interpret them, following standard petroleum FTIR band assignment practice (Speight, 2006).

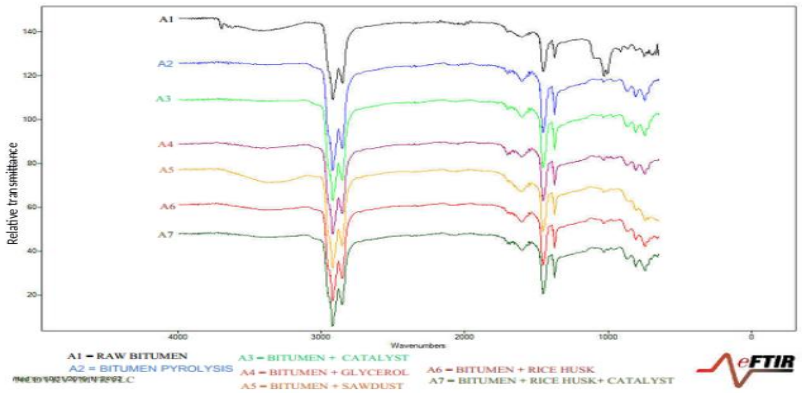



Figure 3: FTIR Spectra of the Raw Bitumen (A1) and the Six Upgraded Products: Bitumen Pyrolysis (A2), Bitumen/Catalyst (A3), Bitumen/Glycerol (A4), Bitumen/Sawdust (A5), Bitumen/Rice Husk (A6), and Bitumen/Rice Husk/Catalyst (A7).

**Table 3: FTIR Wavenumber Assignments Used to Interpret the Liquid Product Spectra**

| Wavenumber ($cm^{-1}$) | Functional group | Compound class |
|---|---|---|
| 3700 to 3584 | O-H stretching | Alcohol |
| 3000 to 2500 | C-H stretching | Alkyne |
| 2140 to 1990 | N=C=S stretching | Isothiocyanate |
| 2000 to 1650 | C-H bending | Aromatic compound |
| 1710 to 1685 | C=O stretching | Conjugated aldehyde |
| 1650 to 1600 | C=C stretching | Conjugated alkene |
| 1465 to 1450 | C-H bending | Alkane |
| 1400 to 1000 | C-F stretching | Fluoro compound |
| 980 to 960 | C=C bending | Alkene |
| 870 to 855 | C-H bending | Alkane |
| 850 to 550 | C-Cl stretching | Halo compound |

Across the seven spectra (raw bitumen and six upgraded products), absorption in the 3700 to 3584 $cm^{-1}$ region confirmed the presence of alcohol O-H groups, while bands in the 2000 to 1650 $cm^{-1}$ region and at 1650 to 1600 $cm^{-1}$ confirmed aromatic C-H bending and conjugated alkene C=C stretching respectively, consistent with the aromatic enrichment also seen in the GCMS results (Section 3.5). Comparing spectra across samples showed that the isothiocyanate associated band (2140 to 1990 $cm^{-1}$, N=C=S stretching) was present in the raw bitumen, the pyrolysis only product, and the glycerol, sawdust and rice husk only products, but was absent from the catalyst only and rice husk with catalyst products, indicating that the catalyst promotes further conversion or removal of this functional group. Conjugated aldehyde absorption (1710 to 1685 $cm^{-1}$, C=O stretching) was present in all products except the sawdust run, in which it was notably absent. These comparisons are qualitative in nature: because sample film thickness was not standardized across the seven spectra and transmittance was not normalized against an invariant reference band (e.g., the 1465 to 1450 $cm^{-1}$ aliphatic C-H bending mode), the FTIR results reported here indicate the presence or absence of functional groups rather than their relative concentration.

**GCMS Compositional Analysis and Aromatic Content Shift**

GCMS analysis identified between 16 and 24 distinct compounds in each sample. Table 4 reports, for each sample, the proportion of total identified peak area contributed by compounds bearing an aromatic (benzene type) ring, based on a name based screening of the compound list. This screening is a practical approximation intended to show the broad compositional trend and not a substitute for full structural confirmation of every listed compound.

**Table 4: Aromatic Ring Bearing Compounds as A Proportion of Total Identified GCMS Peak Area**

| Sample | Number of identified compounds | Aromatic ring bearing compounds (% of total peak area) |
|---|---|---|
| Raw bitumen | 18 | 7.9 |
| Pyrolysis only | 24 | 74.0 |
| Bitumen / Catalyst | 20 | 91.5 |
| Bitumen / Glycerol | 22 | 90.0 |
| Bitumen / Sawdust | 16 | 75.7 |
| Bitumen / Rice husk | 17 | 90.7 |
| Bitumen / Rice husk / Catalyst | 20 | 86.7 |

GC-MS separates and detects only the fraction of each liquid product that can volatilize and elute from the column, typically compounds boiling up to about 300 to 320°C under the temperature programs used here. Raw Agbabu bitumen is dominated (over 70 wt%) by heavy, largely non-volatile resin and asphaltene fractions that remain at the column inlet and

do not elute; the 7.9% aromatic figure reported for raw bitumen in Table 4 therefore describes only the small volatile slice of the feed that reaches the detector, not the bulk composition of the whole sample. Because thermal cracking and catalytic/hydrogen-donor treatment convert part of these heavy, non-eluting fractions into lighter, volatile mono- and di-ring aromatics that do elute, a substantial part of the large apparent rise in aromatic content between the raw bitumen and the upgraded products in Table 4 reflects this shift in what the technique can detect, rather than a directly comparable bulk measurement before and after upgrading.

The raw bitumen was dominated by aliphatic and fatty acid type compounds, such as n-hexadecanoic acid and oleic acid, with aromatic ring bearing compounds accounting for only 7.9% of identified peak area. On pyrolysis alone, this rose sharply to 74.0%, dominated by simple aromatics, such as Toluene and Benzene together with polycyclic aromatics such as Pyrene and Benzo(a)anthracene, indicating that thermal cracking of the bitumen at 350°C strongly favours aromatization. All five further treatments increased the aromatic fraction beyond the pyrolysis only level, with the catalyst only run giving the highest aromatic content of all seven samples (91.5%), followed closely by the rice husk only run (90.7%) and the glycerol run. The combined rice husk and catalyst run gave a slightly lower aromatic fraction (86.7%) than either the catalyst only or rice husk only run individually, with a corresponding increase in the contribution of phenolic and naphthol type oxygenated aromatics, such as p-cresol and 1-naphthol, which points to the hydrogen donor moderating the extent of full aromatization while still supporting extensive ring formation. The presence of phenolic species in the rice husk and sawdust containing products is consistent with the known thermal decomposition behaviour of lignin, the third major structural polymer of lignocellulosic biomass alongside cellulose and hemicellulose; lignin is itself a three dimensional polymer built from propenylphenol and methoxylated propenylphenol structural units, so its thermal breakdown characteristically releases phenol, cresol and related phenolic fragments (Diebold and Bridgwater, 1997). Hemicellulose, the second major structural polymer, is reported to yield proportionally more non condensable gas and less tar on pyrolysis than cellulose (Behrendt et al., 2008), which is consistent with the more rapid pressure rise observed for the rice husk containing runs in Section 3.2 relative to the pyrolysis only and glycerol runs, since glycerol, unlike rice husk and sawdust, contains no lignin or hemicellulose fraction. Considered alongside the physical property results in Section 3.3, this indicates that the superior viscosity reduction and API gravity gain achieved by rice husk combined with catalyst is associated with a liquid product that is highly aromatic but retains a greater share of phenolic oxygenated species than the catalyst only product, rather than with a fundamentally different reaction pathway.

## CONCLUSION

Upgrading of extra heavy Agbabu bitumen (API gravity 8.6°, viscosity 32000 mPa s) by pyrolysis, catalytic cracking, and biomass assisted hydrogen addition using glycerol, sawdust and rice husk, individually and with rice husk combined with an equilibrated zeolite catalyst, reduced viscosity by 90.6 to 94.1% and raised API gravity to between 24.3 and 28.9° across all six routes evaluated. Rice husk combined with catalyst was the most effective treatment on both measures simultaneously (1900 mPa s, 28.9° API), and this ranking, from sawdust as the least effective additive to rice husk with catalyst as the most effective, was identical whether judged by viscosity reduction or by API gravity gain. Reactor pressure and temperature response profiles showed that the rice husk containing runs reached higher pressures and their set point temperature, sooner than the pyrolysis, glycerol or sawdust runs, which is consistent with more vigorous early cracking activity, although this comparison is partly confounded by a difference in stirring between the biomass and non-biomass runs. FTIR and GCMS analysis confirmed a marked shift from an aliphatic, fatty acid dominated raw bitumen toward aromatic, phenolic and carbonyl rich upgraded products, with aromatic ring bearing compounds rising from 7.9% of identified peak area in the raw feed to 75 to 92% across the six upgraded products. Taken together, these results support rice husk, and particularly rice husk combined with a zeolite catalyst, as an effective and low cost renewable hydrogen donor route for upgrading Nigerian extra heavy bitumen.

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