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Co-processing alternative feedstocks through the FCC

Decarbonise your FCC by co-processing alternative feedstocks,
and enhance the incorporation of biogenic carbon in products

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The fluid catalytic cracking (FCC) unit continues to be a significant source of refinery margin, enabling refiners to upgrade the bottom of the barrel to valuable transportation fuels and petrochemical feedstocks while also maximising liquid volume yield. The inherent process flexibility of the FCC enables refiners to react swiftly to changing market economics, ranging from maximising distillate production to maximising petrochemical precursors. However, despite these benefits, the FCC is a major contributor to CO₂ emissions from the refinery, leading operators to consider decarbonisation strategies to help deal with these unavoidable CO₂ emissions.

One approach is to reduce grey carbon intake through co-processing of alternative feedstocks. This allows the FCC energy balance to be respected while also reducing the contribution of fossil fuels to overall CO₂ emissions from coke combusted. FCC co-processing is in its infancy, but several refiners are exploring new feedstocks.

Some of these feedstocks, such as biomass pyrolysis oils, can also help refiners meet RED II advanced biofuel mandates, which currently require transportation fuels to contain at least 3.5% advanced biofuel-derived energy by 2030. Under Annex IX, biomass pyrolysis oil can be double counted, offering a potentially low-cost solution to meet the RED II targets.

Methanol option

Capture and re-use of FCC flue gas, either for sequestration or use as syngas feedstock for production of methanol, provides an additional approach to decarbonise. Methanol has significant potential to become a low carbon energy vector.

Johnson Matthey has developed HyCOgen™, a reverse water gas shift technology that achieves the appropriate CO₂ conversion required for methanol synthesis. Johnson Matthey has a long history in methanol synthesis and flowsheet design.

Various alternative feedstock types are being looked at for co-processing in the FCC. These feed types each have their own unique combination of impacts on FCC yields, selectivities, and unit performance. Potentially important feedstocks and their impact are summarised in Table 1.

Co-processing biomass pyrolysis oils can be a significant challenge in the FCC (see Table 1). Biomass pyrolysis oils are highly unstable due to their significantly high levels of oxygenated compounds. These oxygenates risk polymerisation at the injection nozzles if normal feed temperature and steam partial pressures are applied; however, such challenges can be managed using specifically designed feed nozzles at a separate location in the riser. Pyrolysis oils can contain up to 40 wt% oxygen, which can form excessive amounts of water, CO₂, and CO in the riser. Oxygenates in the form of carboxylic acids are a well-known source of corrosion, which may require upgrading metallurgy in some sections of the FCC.

Examples of feedstocks potentially important for FCC co-processing

Feed	Challenges	RED II targets
Vegetable oils	<ul style="list-style-type: none"> • Oxygenates can be an issue in some cases • Political competition with food sector 	Limited to 7%
Biomass pyrolysis oils	<ul style="list-style-type: none"> • Increased coke selectivity • Increased dry gas selectivity • Immiscible with conventional oil feeds • Thermally unstable • Oxygenates, chlorides, calcium, potassium, etc 	Advanced biofuels >3.5% (Biomass pyrolysis oil can be double counted, effectively lowering the limit)
Waste plastic pyrolysis oils	<ul style="list-style-type: none"> • Chlorides and other contaminants 	No impact

Table 1

Contaminants

Biomass pyrolysis oil is also challenging due to the presence of contaminant metals such as calcium, potassium, and sodium. The detrimental effects of sodium and potassium in the FCC are well known. Sodium and potassium are both basic; hence, they neutralise acid sites in the zeolite and, thereby, permanently deactivate the catalyst. Calcium can also neutralise acid sites, but these tend to be on the catalyst matrix at the outer surface of catalyst particles. Calcium also enhances the deleterious effects of iron by promoting the fluxing of iron and glassy nodule formation in the regenerator.

Recognising the challenges in processing biomass pyrolysis oil led Johnson Matthey to partner with the National Renewable Energy Laboratory (NREL), a national laboratory of the US Department of Energy focusing on renewable energy technology development. NREL provided biogenic feedstock and operated FCC micro-reactor testing equipment.

Collaborative testing

Johnson Matthey provided catalyst design expertise. Microreactors were operated under FCC conditions to observe the extent of biogenic carbon incorporation. Catalysts used included a standard refinery FCC equilibrium catalyst (Ecat) and purpose-made catalysts provided by Johnson Matthey. The objective of the study was to explore the extent of biogenic carbon incorporation into key fuel molecules and evaluate if this could be optimised using appropriate catalyst design.

Conventional VGO (with naturally occurring carbon isotopes, predominantly C^{12}) was utilised as the reference feedstock, while the biogenic feed used consisted mainly of C^{13} carbon isotopes from green oak grown in a C^{13} CO_2 -enriched atmosphere. Due to the significant cost of producing a C^{13} labelled feedstock, the work could only be conducted in micro-reactors.

Use of distinct carbon isotopes for the VGO (C^{12}) and biogenic (C^{13}) feeds provided the ability to track the origin of carbon in products from these feed sources. Gas chromatography (GC) was used to isolate specific key product molecules produced, and then mass spectroscopy (MS) was used to determine from which parent feedstock (C^{12} VGO or C^{13} green oak) the product carbon atoms originated. Further details of these methodologies can be found in *ACS Sustainable Chem. Eng.* 2020, 8, 2652-2664.

Analysis of laboratory data was conducted on a range of different product molecules, including toluene, propylene, 2-pentene, and methylcyclohexane. Similar results were

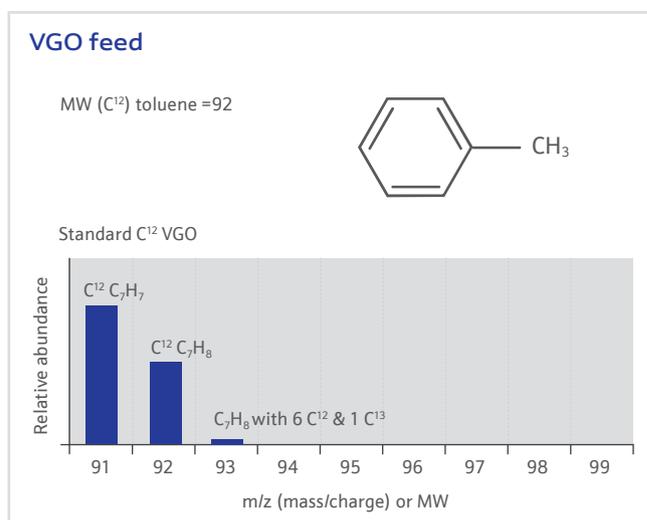


Figure 1: Outcome of GS-MS analysis when VGO is cracked over Ecat

observed for these molecules, but as an example, the focus in this instance is specifically on toluene. Toluene derived exclusively from C^{12} has a molecular weight of 92. In the mass spectrometer, the toluene molecule is ionised, during which fragmentation occurs. The main fragmentation peaks for C^{12} toluene to occur at M/Z (mass/charge) 92 ($C_7H_8^+$) and 91 ($C_7H_7^+$), with the loss of a single hydrogen atom. Any peaks with M/Z of 93 or above must incorporate at least one C^{13} atom. By comparison, toluene derived purely from a C^{13} source has its main fragmentation peaks at M/Z of 99 ($C^{13}C_7H_8^+$) and 98 ($C^{13}C_7H_7^+$). Using GC-MS, therefore, allows for determination of which carbon atoms in product molecules originate from the C^{12} VGO or C^{13} green oak feedstock.

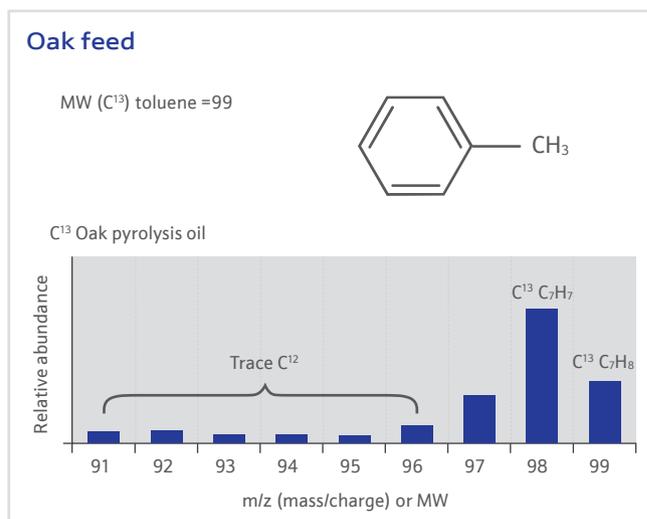


Figure 2: Outcome of GC-MS analysis when biomass green oak is cracked over Ecat

50% VGO + 50% Oak Feed

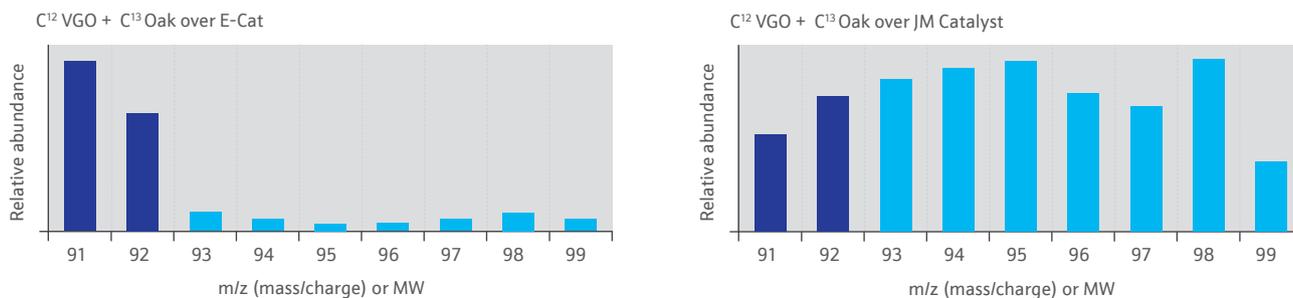


Figure 3: Outcome of GC-MS analysis when a mix 50% VGO/50% oak feed is cracked over Ecat and JM Catalyst

Test runs

Establishing a clear baseline is fundamental to achieving good data, so the first test run was made using 100% VGO (C¹²) over standard FCC Ecat, providing an excellent baseline. The micro-reactor was operated using the same Ecat, operating at the same conditions, but this time using 100% green oak (C¹³) feedstock. Results from these test runs provided clear boundaries where each pure feedstock was used. To explore co-processing, the micro-reactor was operated with a 50:50 wt/wt ratio of VGO and green oak feeds. However, it is recognised that such a high ratio may not be practical in a commercial FCC due to increased delta coke and other operating issues. This 50:50 feedstock was tested using standard Ecat and then tested using equilibrated purpose-made catalysts.

Figure 1 shows the GC-MS spectrum for the baseline 100% VGO/standard Ecat run. The origin of the derived toluene is clearly all attributable to the C¹² source having M/Z peaks at 91 and 92.

Figure 2 shows the results for the 100% green oak over standard FCC Ecat. As expected, the majority of the toluene was derived from the C¹³ source with M/Z peaks at 99 and 98. Some toluene was produced with M/Z peaks lower than 98 due to successive amounts of trace C¹² incorporated because it was not practical to fully isolate all traces of C¹² when growing the green oak from the C¹³ enriched CO₂.

Co-processing runs provided interesting observations that gave insight into how biogenic carbon interacts with conventional oils. Figure 3 shows that the dominant source of carbon atoms in toluene produced over standard Ecat originated from the VGO (C), despite the feedstock being a 50:50 ratio with green oak. To explain this, we consider

that much of the biomass pyrolysis oil was lost to coke production and CO + CO₂ in the dry gas.

Very different conclusions were made when using the purpose-made catalyst, as can clearly be seen in Figure 3. Toluene produced using the purpose-made catalyst showed significantly higher C¹³ incorporation, as seen in the increase in relative abundance of M/Z peaks above 92 (having at least one C¹³ atom). As expected, some toluene was derived from the C¹² VGO source, but overall, toluene from this feedstock was minor. Toluene with an M/Z peak of 99 contained exclusively C¹³, and peaks from 93 through to 98 had successive levels of C¹³ incorporated in the molecular structure. We refer to the mixing of grey and green carbon atoms within molecules as carbon scrambling. The purpose-made catalyst was designed to promote olefin aromatisation and aromatic transalkylation reactions to encourage carbon scrambling in the FCC.

Figure 4 illustrates the reaction mechanism: it shows benzene being produced by aromatisation of two propylene molecules derived from differing carbon sources (grey C¹² and green C¹³). Olefin aromatisation produces aromatic rings that can contain both grey and green carbon atoms. These already carbon-scrambled aromatics can also react with other aromatic molecules to achieve further carbon incorporation through aromatic transalkylation reactions (the exchange of side chains between aromatic molecules).

The results from this study provide the first step towards the development of catalysts specifically designed to improve biogenic carbon incorporation into FCC products. Increasing biogenic carbon incorporation will help refiners meet RED II mandates more easily. The focus of this research was to explore and understand key mechanisms important for biomass co-processing in the FCC and

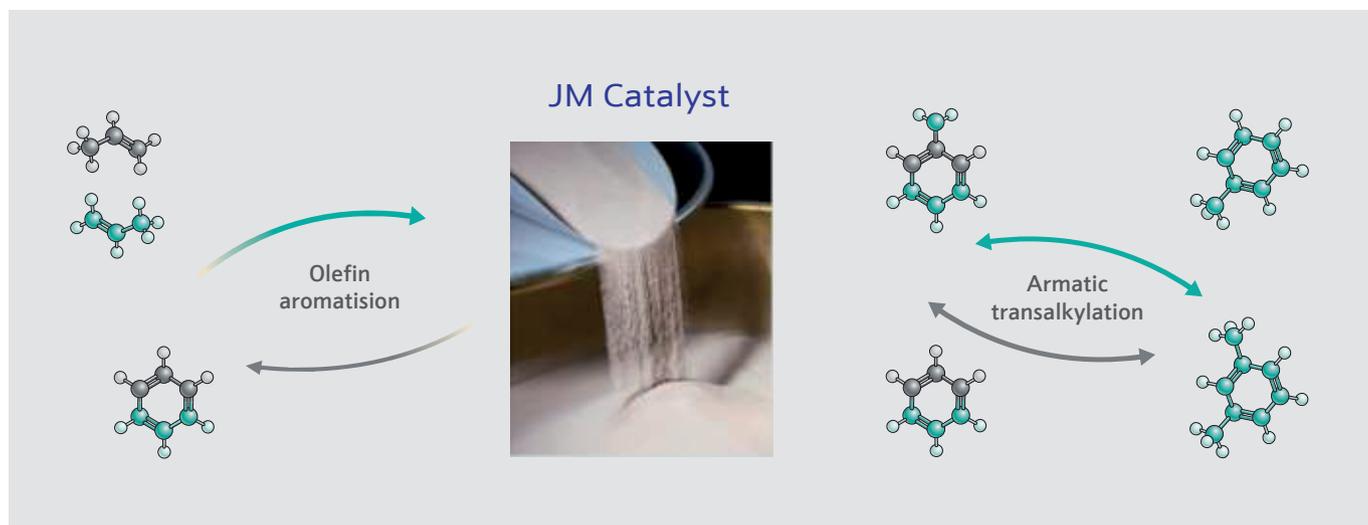


Figure 4: Scrambling toluene mechanism

understand whether the extent of incorporation could be improved by appropriate catalyst design. Due to the expense of C^{13} feedstocks, feed quantities were small; hence, studies were made only at micro-reactor scale. Full yield mass balance was not possible, nor was the intent at this stage. A followup phase II testing programme is currently under way to explore the impact of biomass pyrolysis oil processing from a mass balance and operating perspective at a larger scale.

Conclusion

This technique provided an effective method for tracking biogenic carbon at laboratory scale and can be used to help develop and optimise catalyst design. Standard Ecat achieved little biogenic carbon incorporation, with the dominant source of products containing only C^{12} , despite the feedstock being a 50:50 ratio of VGO and green oak. Purpose-made catalyst significantly enhanced biogenic carbon incorporation in the products.

Co-processing biofeeds in the FCC can be an attractive low capex option for refiners to decarbonise their assets. This study demonstrated that proper catalyst design has the potential to enhance the incorporation of biogenic carbon in products of interest, hence, supporting refiners to meet government mandates on biofuels.

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