

SUMMARY FOR REFINERS: RFO BIOCRUDE ANALYSES AND REACTION PATHWAYS

UOP Honeywell / 2017

Stated as simply as possible, most of the molecules in RFO biocrude fall within the gasoline/diesel boiling range once they are deoxygenated in the FCC, and a typical RFO biocrude already has 40 to 50% of its make-up boiling in the gasoline or lighter range. More significantly, a full 75% of the biocrude material, whose boiling point is under 550 F, will end up in the gasoline and lighter cut simply when deoxygenation occurs in the FCC riser. The reaction conditions of the FCC riser act to deoxygenate and “clean up” the biocrude-derived gasoline and diesel range material, making it suitable for blending into standard hydrocarbon transportation fuels. As outlined below, even the aromatic rings, since they are connected by aliphatic bonds in the biocrude, can be easily cracked to hydrocarbon fuels.

The FCC riser is surprisingly well adapted to handle the types of oxygenated molecules that are present in biocrude, and what happens chemically as biocrude is converted and reacts with petroleum in the riser, is summarized as follows.

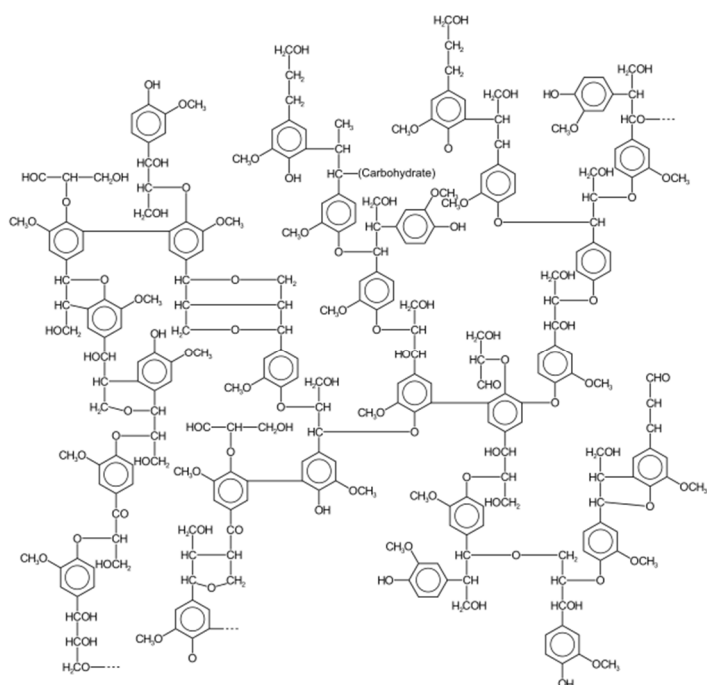
RFO biocrude from wood is mainly depolymerized cellulose and hemicellulose. These compounds, are polymers of glucose, a non-aromatic ring structure, and therefore do not tend to produce aromatic rings via the initial pyrolysis step (i.e., when produced initially, before conversion in the FCC riser). Instead they yield primarily C6's and shorter aliphatic oxygenates, which are very “crackable” in an FCC riser. These oxygenates include methanol, organic acids, acetol, other carbonyls, dehydrated sugars and larger carbohydrate polymers. All of these aliphatic substances have oxygen functional groups or linkages that the FCC catalyst removes by decarboxylation and dehydration reactions. Oxygen atoms in the aliphatic chains produce reactive centers where chain-breaking reactions occur and conversely, also form longer chains via Diels-Alder and Aldol condensation mechanisms. The chain growth mechanisms explain how a feed that has up to 40% molecules with carbon chain lengths less than six yields very little dry gas and LPG, instead condensing to gasoline and diesel boiling range products. A typical overall breakdown of the various types of materials in RFO can be found in Table 1.

Table 1 Typical RFO Composition

Compound Class	Composition Range (wt.%, water free)
C1 compounds (formic acid, MeOH, CO₂,	5-10
C2-4 substituted linear aldehydes and ketones	15-35
Substituted furans, furanones and pyranones (C5-C6)	10-20
Anhydrosugars (incl. oligosaccharides)	6-10
Water soluble carbohydrate derived polymers	5-10
Monomeric methoxy -substituted phenols	6-15
Pyrolytic Lignin /Ligninic-derived aromatics	15-30
From D. Radlein in Bridgewater, 1999 as referenced by Oasmaa et al, VTT Publications 2001.	

RFO biocrude-derived aromatics originate from the lignin part of the tree. Lignin is an aromatic polymer of ether-linked methoxy phenyls with propyl and propanol substituents as shown below in Figure 1. When these are pyrolyzed to produce RFO biocrude, a mix of phenolic and polyphenolic compounds are produced, as listed in Figure 2. Very few of these compounds are condensed PNA's or biphenyls, as are found in VGO. These polyphenols are typically linked by an aliphatic carbon or ether linkage, which when introduced into the FCC riser, are easily cracked over an acid FCC catalyst producing cuts in the gasoline and diesel range. As a result of the existence of these crackable linkages in RFO biocrude, heavy aromatics in the biocrude are more easily reduced in molecular weight than is the case with the PNA's, such as the anthracenes or phenanthrenes that are found in VGO. These PNA's in the VGO simply do not have reactive carbons sites for the acid catalyst to act on. Since aromatics in RFO biocrude are not PNA's and do not behave in the same way as aromatics in VGO, they crack much more easily to mono-aromatics in the FCC riser, yielding products in the gasoline and diesel range.

Figure 1 Lignin structure



In summary, the majority of the molecules making up RFO biocrude are not actually aromatic, and those that are aromatic, are not PNAs but are phenyl groups linked by aliphatic carbons and ethers. These can be readily cracked to yield monoaromatics in the naphtha and LCO/diesel range.

The FCC catalyst dehydrates and decarboxylates the oxygenates, yielding pure (de-oxygenated) hydrocarbons. The most difficult of these reactions is the dehydration of phenols and deoxygenation of the lower molecular weight ketones, which is why the phenols and acetone are the last to be fully converted. Any unconverted phenols end up primarily in the FCC naphtha with those phenols that are

native to the FCC, and that are produced from oxygen which is entrained along with VGO aromatics. Phenols are known to improve the stability of the gasoline.

Finally the existence of acids, aldehydes, alcohols and furans provide reactive centers for chain growth mechanisms to occur, allowing short carbon chain lengths to grow and form molecules in the naphtha range.

Figure 2 Pyrolyzed Lignin Fragments

