

# Co-processing renewable and recyclable feedstocks in the FCC unit

As new regulations drive refiners to develop more sustainable processes to produce fuels and chemicals, they are exploring co-feeding renewable and recyclable feedstocks

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While the refining industry currently plays a vital role supplying much of the world's transportation fuels and commodity chemicals, new regulations are forcing them to produce fuels and chemicals more sustainably. As a result, refiners have begun exploring co-processing renewable and recyclable crude oils (RCOs) to replace conventional fossil based feedstocks. The new feeds present challenges such as additional metal contaminants and differences in feedstock chemistry. The ability of the FCC unit to manage metal contaminants and tolerate a wide variety of feedstock makes this process well suited to co-process these RCOs.

At BASF, we are exploring alternative feedstocks, their implications on the operation of the FCC unit, and how the catalyst can be designed to address the new challenges that will be created. Through collaborations and partnerships, we have access to a diverse collection

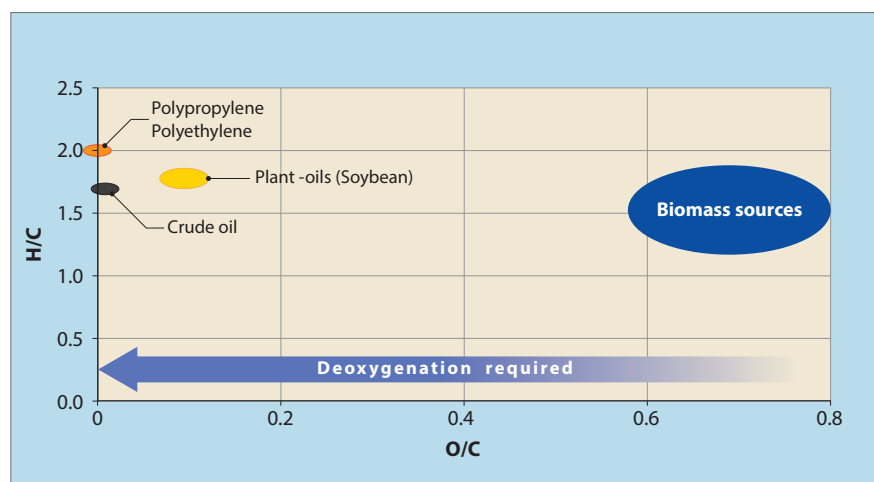
of RCOs, as well as the resources needed to prepare custom RCOs. We have also adapted our existing catalyst testing laboratories to explore how these new feedstocks will behave in FCC units.

## Challenge of RCOs

RCOs originate from three possible sources: pyrolysis of recyclable waste streams such as plastics and tyres, plant based oils such as soybean oil and corn oil, and pyrolysis of biomass such as wood residues and corn stover. Depending on the source and the conditions used to prepare the RCO, the properties will vary considerably. On one end of the spectrum, pyrolysis oils derived from polyethylene and polypropylene wastes contain high hydrogen to carbon and minimal oxygen content. This makes oil produced from these materials easily upgradable. In contrast, pyrolysis oil derived from biomass will present challenges due to its inherently lower hydrogen to carbon content,

significantly higher oxygen content, and relatively high content of alkali metals. Between these two extremes will be plant based oils containing moderate content of oxygen and alkali metal contaminants.

One way to illustrate the diversity of the different feedstock options is to examine their differing carbon, hydrogen, and oxygen content, which is illustrated in a Van Krevelen diagram in **Figure 1**. The lower the hydrogen to carbon (H/C) content of the feedstock, the more challenging it will be to upgrade into transportation fuels and chemicals. For reference, H/C content of petroleum based crude oil is roughly 1.7. The relatively high H/C content of polyethylene and polypropylene (~2.0) makes these ideal starting points for deriving RCOs. While biomass appears to have a H/C content similar to petroleum based oil, the other factor that must be considered is the oxygen to carbon content (O/C). A lower O/C results in a feed that is easier for refiners to process. **Figure 1** shows that biomass based and plant-derived oils have a higher O/C than crude oil. In plant-derived oils, oxygen is contained within the structure of the triglycerides comprising the oil. While sources of biomass wastes will vary, all are comprised of lignin, cellulose, and hemicellulose that are rich in oxygen. In an FCC process, the oxygen contained in biomass pyrolysis oils and plant oils will be removed through various deoxygenation pathways producing  $H_2O$  (hydrodeoxygenation),  $CO$  (decarboxylation), or  $CO_2$  (decarbonylation), all low-value products for refiners.



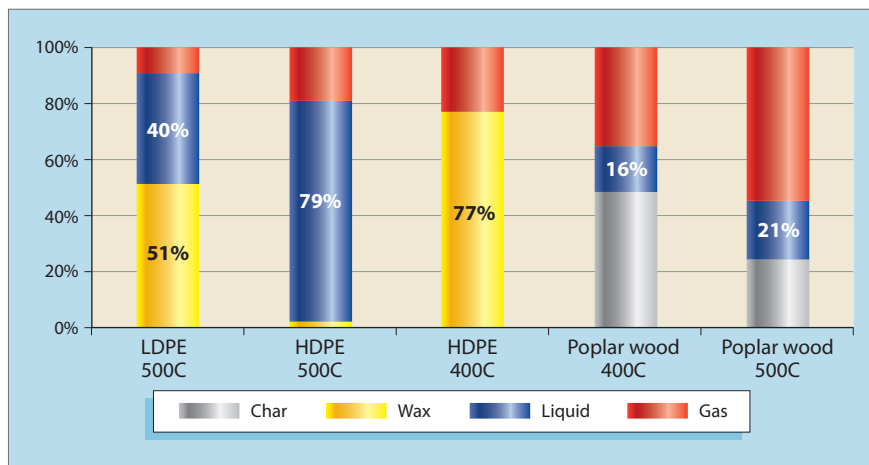
**Figure 1** Van Krevelen diagram illustrating the diversity of the different RCO feedstocks in terms of their carbon, hydrogen, and oxygen content relative to conventional crude oil

However, in addition to increasing gas yields, deoxygenation will influence yields of high-value products, depending on which pathway is dominant. Producing more CO/CO<sub>2</sub> will consume carbon that otherwise could be used to make fuels and chemicals. Producing more H<sub>2</sub>O will consume hydrogen, reducing the effective H/C, and potentially increase the tendency to form coke.

New metal contaminants will also create challenges when processing RCOs. Plants are rich in alkali metals that will be carried over into biomass based pyrolysis oils and plant based oils. Similar to metals contained in conventional oils, the alkali metals will accumulate on the surface of the FCC catalyst, requiring new metal passivation strategies to be incorporated into the design of the catalyst. The extent of alkali metal contaminants will also vary with the source of the RCO. On one end of the spectrum will be plastic-derived oils with little or no contaminant metals. On the other end of the spectrum will be oils derived from biomass pyrolysis that will potentially have a significant content of alkali metals such as Ca, K, Mg, and Na.

### Pyrolysis of renewable and recyclable materials

Understanding the process of pyrolysis is important in understanding the nature of different RCOs and how they will behave during co-processing in a refinery. Pyrolysis is a process involving the thermal decomposition of materials at elevated temperatures in an inert atmosphere. Pyrolysis results in the formation of a broad spectrum of hydrocarbon fragments that can be categorised by condensation temperature: waxes comprise products condensing at or above 25°C, liquids comprise products condensing between -15°C to 25°C, and gases are products condensing below -15°C. A fourth product category is char, which consists of a highly carbonaceous non-volatile residue forming in the pyrolysis reactor. The yields of gases, liquids, wax, and char will vary based on the design of the pyrolyser, pyrolysis conditions, and the material being



**Figure 2** Results from lab-scale pyrolysis illustrating the influence source and pyrolysis conditions will have on yields from pyrolysis

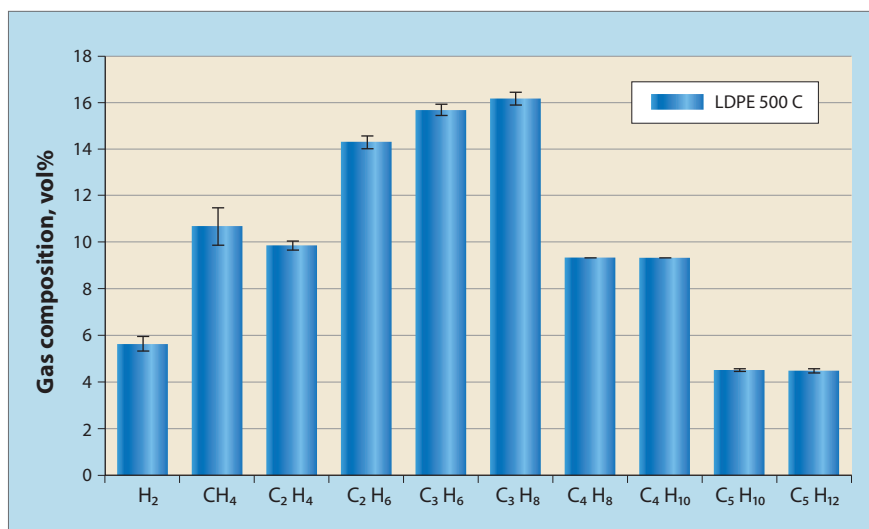
pyrolysed. As one example of this variation, **Figure 2** shows pyrolysis yields from a lab-scale pyrolysis unit for varying materials and pyrolysis temperatures. In general, the amount of upgradable products from plastics will be significantly more than that obtained from biomass.<sup>1</sup> In the lab-scale results illustrated in **Figure 2**, plastic pyrolysis yielded 80-90% upgradable products (liquids and wax) compared to biomass pyrolysis yielding only 15-20% upgradable product (liquid).

### Plastic pyrolysis oils

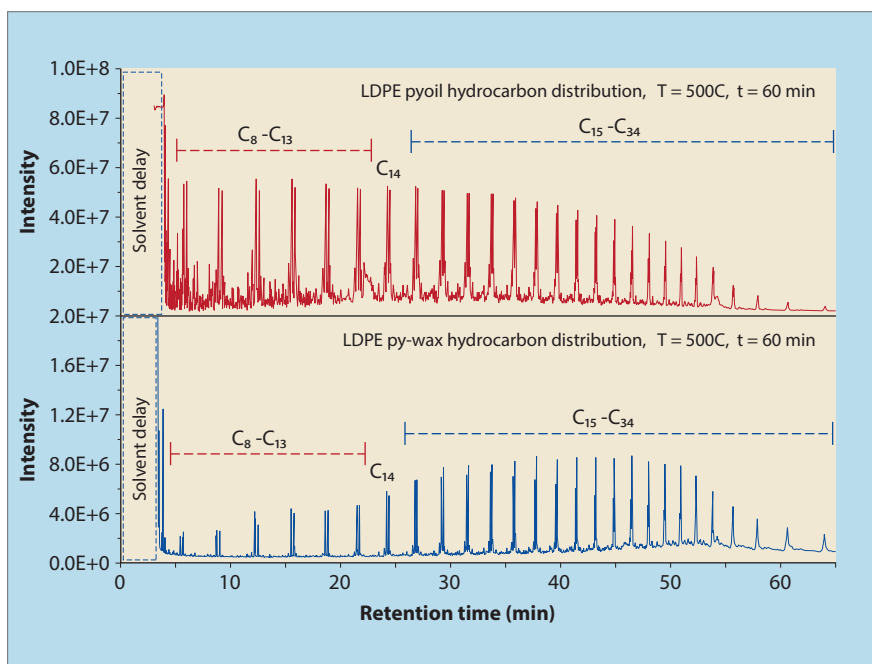
While any plastic can be pyrolysed to produce an oil, polypropylene and polyethylene are more commonly used as feedstock for commercial production of plastic-derived pyrolysis oil, as they produce oil well suited for upgrading. When these plastics undergo pyroly-

sis, the large hydrocarbon polymers are thermally cracked into a very broad distribution of smaller hydrocarbon fragments. Using the lab-scale pyrolysis oils shown in **Figure 2** as an example, the pyrolysis of low density polypropylene (LDPE) yields a range of hydrocarbons from methane to C<sub>34</sub> size hydrocarbons. In this experiment, the gas fraction contained hydrocarbons from methane to pentane (**Figure 3**). The liquid and wax fractions were comprised of hydrocarbons ranging from light naphtha to C<sub>34</sub> size hydrocarbons, with the wax generally containing a larger portion of the heavier hydrocarbons (**Figure 4**).

Certainly, the heavier portions of the liquid and wax fractions can be easily co-processed with conventional gasoil in FCC. While significantly lighter than conven-



**Figure 3** Composition of gas products from lab-scale pyrolysis of LDPE



**Figure 4** Composition of liquid and wax products from lab-scale pyrolysis of LDPE

tional gasoil, it is possible that the lighter portions of the liquid and wax could be co-processed as well, assuming the impact of the lighter feed on product yields can be tolerated. Both fractions can be readily mixed with gasoil without miscibility issues. When co-feeding plastic pyrolysis oil in a lab-scale ACE unit, the impact of the lighter feedstock results in higher yields of LCO, gasoline, and LPG yields consistent with the percentage being co-processed. Otherwise, the co-processing of plastic pyrolysis oil does not negatively impact yields.

### Plant based oils

Plant based oils such as corn oil and soybean oil are extracted directly from the plant. These oils consist of a mixture of triglycerides, which are large molecules comprised of glycerol and three long-chain fatty acids. Different oils will contain different mixtures of triglycerides, but all plant oils will contain long-chain fatty acids and an overall carbon number in the order of 50. While containing a mixture of triglycerides, the distribution of different molecules in plant based oils will be significantly narrower than oils produced by pyrolysis. As a feedstock, several processing options exist to upgrade vegetable oils into fuels and chemicals including co-processing in FCC.<sup>2</sup>

The oxygen contained in the glycerol and fatty acid combined result in an overall oxygen content of roughly 10-15%. In the FCC riser, the majority of this oxygen will be converted to CO, CO<sub>2</sub>, and H<sub>2</sub>O through the deoxygenation pathways discussed above. Depending on which pathway is followed, either carbon will be consumed, resulting in less carbon being available for formation of desired products, or hydrogen will be consumed, potentially increasing selectivity to coke. Which pathway is dominant is a function of the chemistry occurring on the surface of the catalyst. When co-processing plant oils in a lab-scale ACE unit, the yields of LPG, gasoline, or LCO will generally decrease as the result of producing CO and CO<sub>2</sub>. Similar to plastic pyrolysis oils, plant oils also blend well with gasoil without significant miscibility issues.

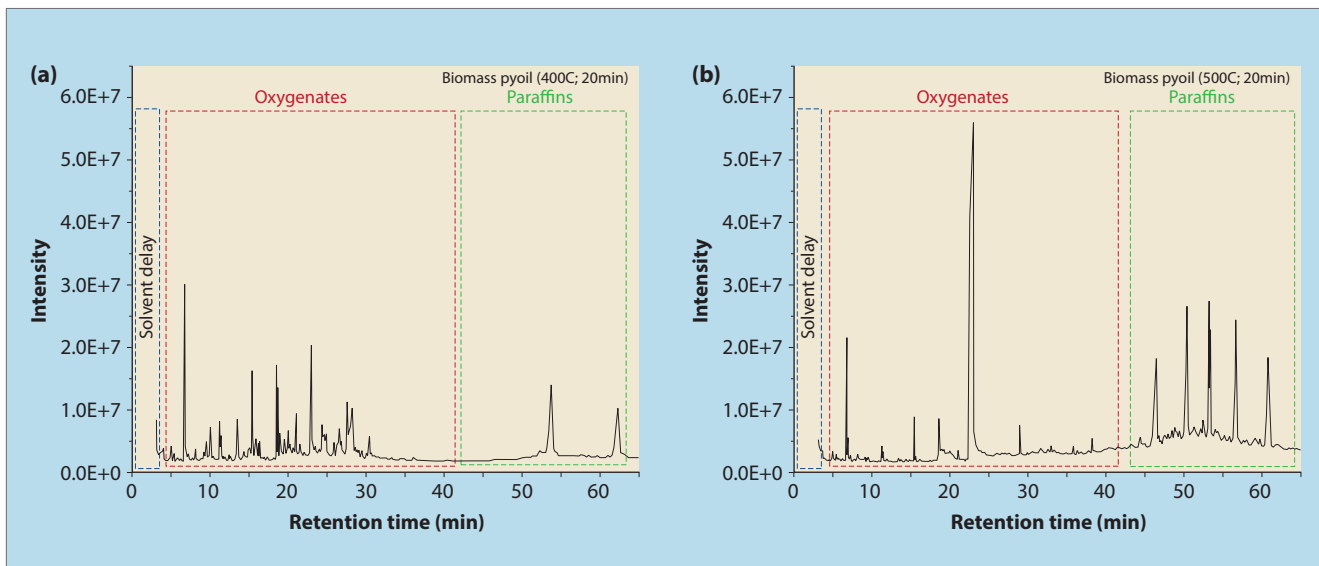
### Biomass pyrolysis oil

Similar to plastic wastes, biomass based wastes can also be pyrolysed to produce hydrocarbon based liquids as an alternative to conventional feedstocks. Examples of biomass waste include a variety of different materials such as corn stover, wheat straw, or wood cuttings and residues. Similar to plastic, the products of pyrolysis will include gases, liquid/wax, and

char.<sup>3</sup> For biomass, formation of char during pyrolysis is inevitable and can represent a significant fraction of the overall pyrolysis yields. The composition of the biochar will be a mixture of inorganic materials originating from the plant material combined with highly carbonaceous residue with the appearance similar to charcoal. The conditions used for pyrolysis will dictate the carbon content of the char, with higher pyrolysis temperature and longer time driving more carbon from char into liquids with the consequence of also increasing yield of gases – also illustrated in **Figure 2**.

While there are many different possible sources of biomass, all biomass will be comprised of lignin, cellulose, and hemicellulose that are rich in oxygen. Typical oxygen content for biomass wastes is 40-45%, which is roughly four times the oxygen content of plant based oils. Between the pyrolysis process and co-processing the resulting liquids in an FCC unit, virtually all of the oxygen contained in biomass will undergo deoxygenation to form CO, CO<sub>2</sub>, and H<sub>2</sub>O. How much deoxygenation occurs during pyrolysis, which depends on the conditions used for pyrolysis, dictates how much oxygen will be contained in the RCO. During pyrolysis, biomass will initially decompose to form smaller hydrocarbon fragments and oxygenates. The oxygenates will then undergo deoxygenation, where higher pyrolysis temperature will generally result in deeper deoxygenation. For example, in the lab-scale results illustrated in **Figure 2**, the amount and diversity of oxygenates is observed to decrease as the pyrolysis temperature is increased due to the higher reaction temperature driving deeper deoxygenation (**Figure 5**).

Ultimately, the liquids from the pyrolysis process will become the feedstock to be co-processed in the FCC unit. These RCOs will be a mixture of hydrocarbons and oxygenates. In the FCC riser, the deoxygenation process that started during pyrolysis will be completed as oxygen is converted to CO, CO<sub>2</sub>, and H<sub>2</sub>O through the same path-



**Figure 5** GCMS spectra illustrating changes in poplar wood pyrolysis oil composition as pyrolysis temperature increases from (a) 400°C to (b) 500°C

ways described previously. The dominant deoxygenation pathway will be important due to the relatively high oxygen content in the RCO. Hydrodeoxygenation to produce H<sub>2</sub>O will consume hydrogen, reduce the effective H/C, and potentially increase coke yield. Decarboxylation to CO<sub>2</sub> or decarbonylation to CO will consume carbon that otherwise could be used to produce more desired product. While deoxygenation is inevitable, the design of the catalyst may be able to influence which pathway is dominant.

## Conclusion

As new regulations drive refiners to develop more sustainable processes to produce fuels and chemicals, they are exploring co-feeding renewable and recyclable feedstocks. The properties and upgradability of these alternate feedstocks will be diverse and very dependent on the origin and process used to prepare the RCO. Unsurprisingly, the FCC unit will be valuable for upgrading these diverse feeds into fuels and chemicals, as the FCC unit has been an asset in the refinery for its ability to tolerate variability in feedstock properties for the last 70 years. Similarly, the correct choice of FCC catalyst will be needed to process this ever-changing feed slate, and, at BASF, we remain committed to creating chemistry to enable refiners

as they transition to more sustainable solutions.

## References

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