

Transforming refineries' opportunities through FCC

Pursuing a sustainable path for recycled and renewable feedstocks

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The integration of recycled and renewable waste streams into chemical value chains is a challenging topic driven by the need to make circularity in the production of chemicals and fuels a reality. Increased circularity in manufacturing will come from both chemically recycling fossil carbon from waste streams such as plastics or tyres and inserting renewable feeds such as lipid-based oils or oils from biomass wastes into refining processes.

Using existing refinery processes for upgrading these materials will offer the opportunity to reduce implementation costs and allow for a gradual transition from conventional oils. However, the properties of oils derived from recycled and renewable wastes will vary considerably and, in some cases, depart significantly from the properties of conventional oils. Some feedstocks will be much more challenging to integrate into existing refinery assets.

One process available to many refiners is fluid catalytic cracking (FCC). For more than 80 years, the process has proven valuable for converting heavy, low-value fractions of conventional oil into high-value products. Inherent in the design and operation of the FCC is a flexibility that will be valuable for upgrading renewable and recycled feedstocks. The combination of continuous catalyst regeneration, periodic catalyst replacement, and flexible catalyst design will

make the FCC process an attractive choice for introducing the new feedstocks into the refinery, particularly for the more challenging oxygenated feedstocks not suitable for other refinery processes.

As more refiners begin to explore the incorporation of renewable and recycled feedstocks into their refining networks, a detailed study of the chemistry associated with these different feedstocks and the implications it will have on refinery processes and needs for new catalytic materials to enable refiners to achieve their sustainability targets are discussed herewith.

Chemistry of sustainable feedstocks

Renewable and recycled feedstocks can be derived from many organic-based wastes. The chemistry of these different wastes can vary considerably and impact how easily different materials can be converted into desired products. On one end of the spectrum will be polyolefin pyrolysis oils and Fischer-Tropsch waxes, having characteristics similar to conventional oil, making them more easily integrated into existing refinery processes.

On the other extreme, highly oxygenated oils derived from biomass will behave much differently than conventional oils, potentially requiring significant pretreatment or

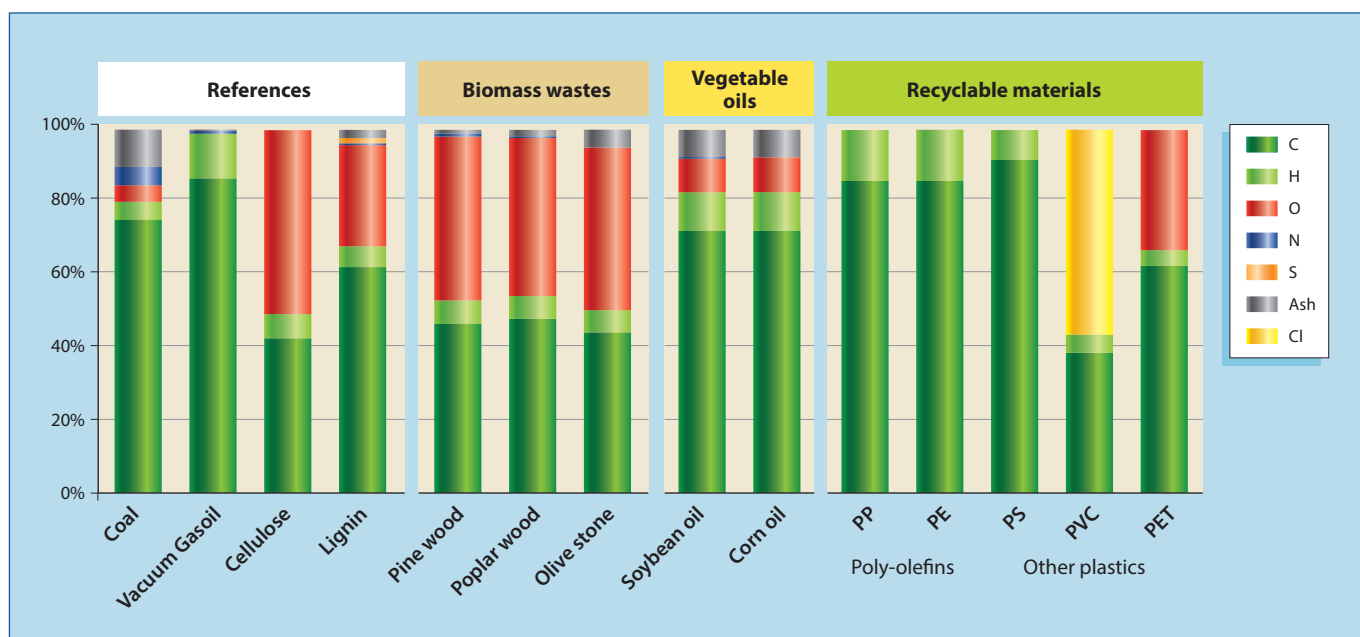


Figure 1 Ultimate analysis of various sustainable feedstocks illustrating carbon, hydrogen, heteroatom, and ash content

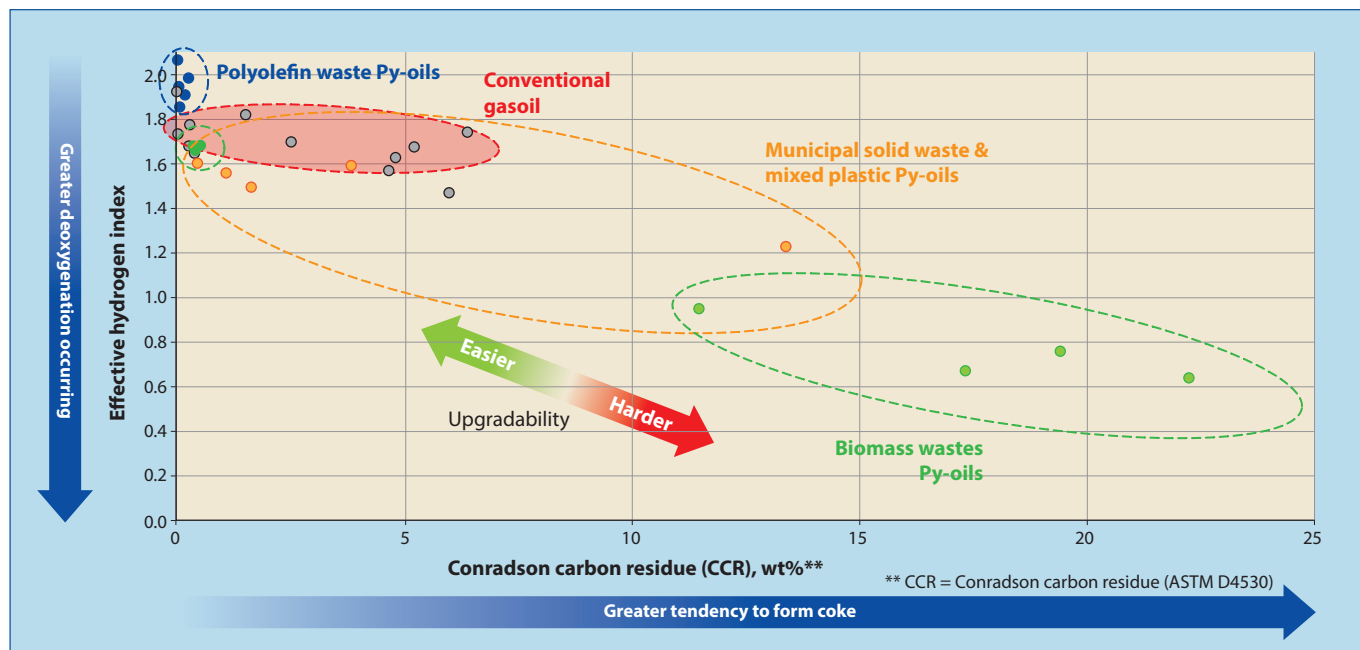


Figure 2 Upgradability of various sustainable feedstocks defined in terms of effective hydrogen index and concarbon

pre-processing prior to introduction into traditional refinery processes. Between these extremes will exist many other possible feedstocks derived from different materials and prepared using different processes. Given this diverse spectrum of possible feedstocks, it is imperative to understand how the underlying feedstock chemistry will drive upgradability so we can better predict how various oils will behave in the refinery.

As with conventional oils, the ultimate analysis of the feedstock gives insights into upgradability (see **Figure 1**). In principle, evaluating the ultimate analysis is the same as that used for conventional oils. It is the carbon and hydrogen that are needed to make products, and higher hydrogen is associated with more easily upgradable feedstocks. Heteroatoms, such as oxygen and nitrogen, are undesirable, and their presence in these new feedstocks will in some cases be dramatically higher than what is found in conventional oil.

Metals making up the ash are also undesirable. In the case of metals, not only could the concentration be higher than what is typically found in conventional oils, the metals will be different. For example, biomass is commonly associated with relatively high concentrations of alkali metals such as sodium and potassium. The implication of these new metals getting incorporated into these new feedstocks will be the need for demetallation processes or new passivating materials incorporated into catalysts.

As with conventional oils, more hydrogen-rich feedstocks will be converted into desired products more easily. In the case of fuels, the relative hydrogen to carbon of the fuel is roughly '2'. The lower the hydrogen content is below 2, the more hydrogen will either need to be added via hydrotreating or carbon rejected via catalytic cracking to produce fuels. For conventional oils, the hydrogen-to-carbon is typically 1.7.

In the case of feedstocks derived from some renewable and recycled materials, the relatively high concentration of heteroatoms has the potential to reduce the effective hydrogen content as heteroatoms are removed from the hydrocarbon.

For example, oxygen removed by dehydration can produce water, which consumes hydrogen. To account for the impact of heteroatoms on hydrogen content, the 'effective hydrogen index' can be defined.¹

$$\left[\frac{H}{C}\right]_{eff} = \frac{H - 2O - 3N - 2S - 1Cl}{C}$$

The effective hydrogen index will vary considerably for different waste streams (vertical axis of **Figure 2**). On one of the spectra will be polyolefin waste plastics that structurally exist as extremely long-chain saturated aliphatic hydrocarbons with zero heteroatoms, resulting in an effective hydrogen index of 2.0, which is higher than conventional gasoil. Upgrading these materials will be relatively easy. On the other end of the spectrum will be oils derived from biomass with an absolute hydrogen to carbon of only ~1.5. However, due to its high content of oxygen, oils derived from these materials will have a very low effective hydrogen index of around 0.5, making upgrading challenging.

A more complete picture of upgradability can be obtained by also considering the Conradson Carbon Residue (concarbon). Conradson Carbon Residue is a laboratory test widely used in the refining industry to provide an indication of the coke-forming tendency of an oil. We can combine concarbon with the effective hydrogen index as a cross plot (see **Figure 2**) to give us a more complete picture of the upgradability of various oils. In **Figure 2**, more easily upgradable feedstocks will be those with higher effective hydrogen and lower concarbon content (upper left corner of cross plot). Conversely, more challenging feedstocks will be those with lower effective hydrogen and higher concarbon content (bottom right of cross plot). Thus, by knowing where a particular feedstock falls within this two-dimensional space, an assessment can be made of its upgradability.

For reference, conventional FCC feedstocks are included in **Figure 2** as well. Refineries have been designed around

the properties of conventional oils. The closer a renewable or recycled feedstock falls in Figure 2 relative to conventional gasoils, the more easily these feedstocks can be upgraded in existing refinery processes. The further a feedstock falls from conventional oils in Figure 2, the more challenging it will be to upgrade in existing refinery processes.

For the specific case of FCC units, as hydrogen content decreases and concarbon increases, the coke yield during cracking will inevitably increase. At some position in Figure 2, there exists a minimum effective hydrogen index and maximum concarbon content, where if the feedstock were fed undiluted into the FCC unit, the coke yield would exceed what the heat balance can tolerate. At this point, the feedstock must be diluted in conventional oil ('co-processing') to increase the hydrogen content and reduce the concarbon of the blend. The lower the effective hydrogen and higher the concarbon content, the more dilution with conventional oil is needed. For example, in the case of biomass pyrolysis oils that have not been hydrotreated, the maximum concentration of bio-oil in gasoil is typically ~10 wt%.

Circular manufacturing of plastic wastes opportunities

Circular manufacturing of plastic has received significant attention over the past decade to reduce the amount of conventional oil needed for new polymer production. One approach applicable to a variety of plastics uses thermal pyrolysis to first convert the solid waste plastic into a hydrocarbon oil, followed by further conversion of the oil into a monomer using existing refinery assets. Due to its relatively high selectivity to producing light olefins and widespread availability, steam cracking is often preferred. However, two limitations of steam cracking are its need for relatively saturated feedstock and hydrocarbons lighter than ~C₂₂ to control the coking rate. Hydrotreating and hydrocracking are possible solutions to manage these limitations, but they add cost. FCC may also be an attractive choice to improve the processability of pyrolysis oils or perhaps even be used as an alternative process to steam cracking.

Polyolefins (polypropylene, LDPE, HDPE) will be the easiest plastic waste for circular manufacturing given its very high hydrogen effective index and very low concarbon, reflected in its location in the top left of Figure 2. During pyrolysis, polyethylene and polypropylene undergo random

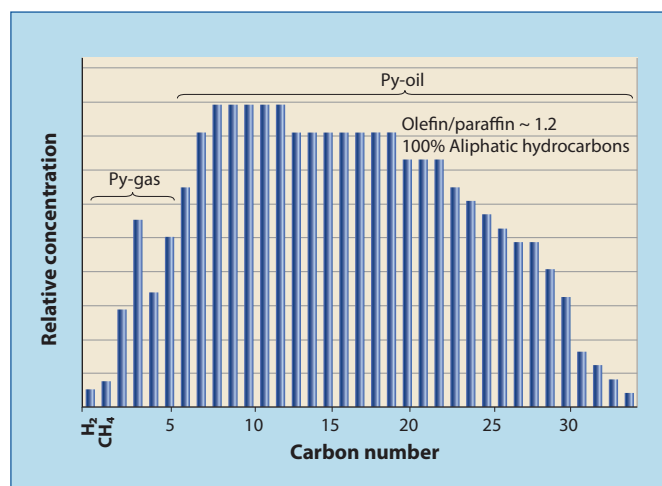


Figure 3 Composition of oil derived from pyrolysis of LDPE plastic measured using combination of chromatography and mass spectrometry

scission, resulting in a broad distribution of largely aliphatic hydrocarbons (olefin/paraffin~1.25) ranging from light gases to heavier waxes (~C₃₄) shown in **Figure 3** for pyrolysis of LDPE. Given the properties of the pyrolysis oil, these oils could possibly be fed into the FCC unit without diluting with gasoil. For example, **Figure 4** shows the case where the LDPE oil described in Figure 3 was fed undiluted into a proprietary ACE reactor using two commercial BASF catalysts: (1) catalyst designed to maximise conversion to naphtha, and (2) catalyst designed to maximise conversion to light olefins.

An ACE reactor is the industry-accepted laboratory-scale process widely used to predict how different catalysts and feedstocks might behave in an actual FCC unit. As would be expected given the properties of the oil, the coke yield is much lower than what is typical for conventional gasoil. In both cases, the wax fraction of the pyrolysis oil is fully converted into naphtha and LPG hydrocarbons.

In the case of the 'Max LPG' catalyst design, more than half of the original pyrolysis oil is converted into relatively olefinic LPG, with the remaining oil being naphtha that could be separated and separately cracked to complete the recycling process. It is worth noting that the coke yield observed in these experiments is so low that traditional FCC with continuous catalyst regeneration may not be required. Rather,

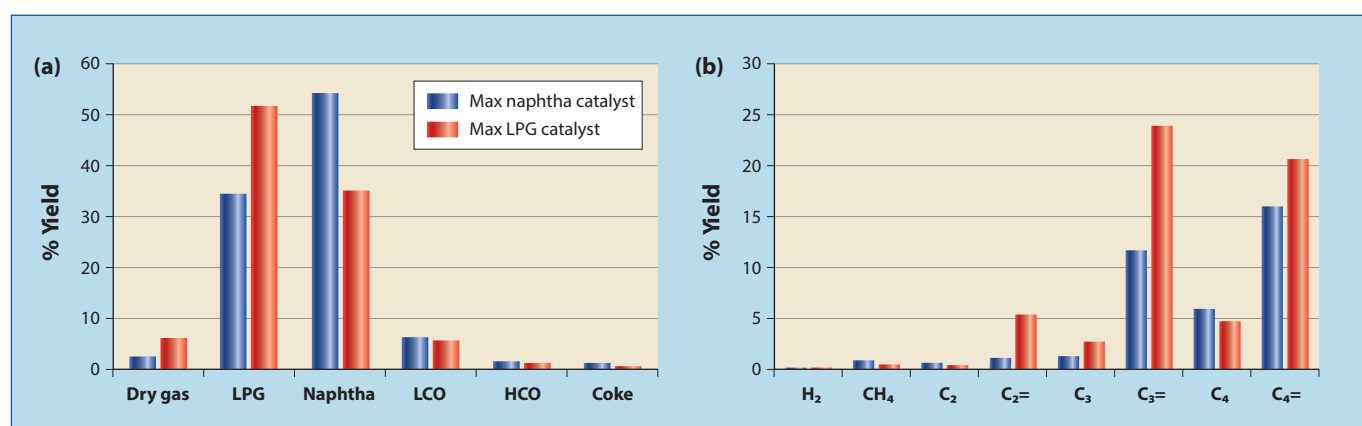


Figure 4 Comparison of (a) overall yields and (b) LPG & dry gas breakdown for catalytic cracking of undiluted pyrolysis oil derived from LDPE using catalyst designed for maximum naphtha and maximum LPG

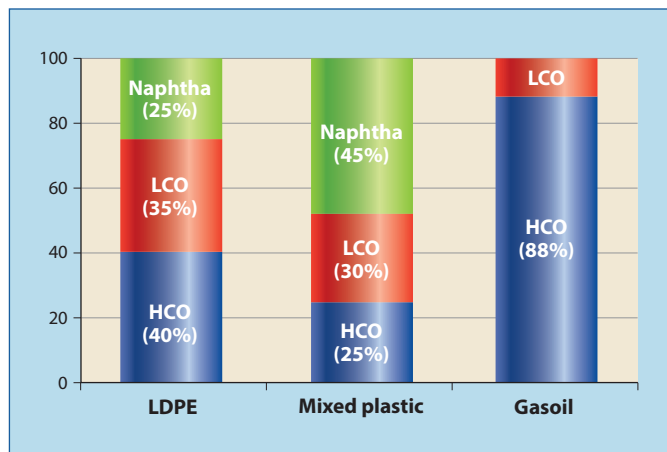


Figure 5 Composition of pyrolysis oils derived from pure LDPE and actual urban mixed plastic waste compared to conventional gasoil

it may be possible to apply a fixed bed catalytic process, which has the potential to significantly simplify the process, allowing integration into the pyrolysis process itself (ex-situ catalytic pyrolysis).

While polyolefins are the most straightforward plastic waste, they only represent 45% of the total available plastic waste generated each year. Further, it will not be practical to completely sort polyolefins from other plastics. Pyrolysis and further upgrading of mixed plastics will be more challenging than polyolefin-based wastes.² For example, polystyrene will undergo non-random scission during pyrolysis, largely yielding only alkylbenzenes, increasing the aromatic content of the oil.

As another example, pyrolysis of polyethylene terephthalate (PET) results in relatively low liquid yields that largely contain benzoic acid, introducing both oxygenates and aromatics into the pyrolysis oil. In practice, streams of plastic waste will be made up of a mixture of materials. Even if polyolefins are desired, complete sorting will not be practical, and some level of other plastics will always be present.

For mixed plastic wastes, the tolerance of the FCC unit to lower hydrogen content and higher concarbon feedstocks may offer an advantage.

BASF has partnered with Neoliquid to explore the upgradability of mixed plastic waste using catalytic cracking. Neoliquid operates commercial-scale pyrolysis units in Spain, preparing oils from a variety of renewable and recycled wastes. ACE evaluation was performed using an oil prepared from a residential mixed plastic waste stream characterised by an effective hydrogen index of 1.5 and a concarbon of 1.0 consistent with a mild conventional resid oil. The composition of the oil measured using simulated distillation via gas chromatography (GC) compared to that associated with polyolefin pyrolysis oil and conventional gasoil is illustrated in **Figure 5**.

A more detailed analysis of the oil using GC combined with mass spectroscopy revealed evidence of several plastics, including polyethylene, polypropylene, polystyrene, and polyethylene terephthalate (see **Figure 6**). In the ACE reactor, the pyrolysis oil was fed undiluted using the commercial BASF max naphtha catalyst, resulting in the yields illustrated in **Figure 7**. Consistent with the design of the catalyst used in this experiment, the pyrolysis oil was converted into a largely naphtha product mix but also contained a significant fraction of olefinic LPG. The coke yield of roughly 4% is in line with conventional mild resid and consistent with the concarbon of 3.9%. Compared to the cracking of pure polyolefin pyrolysis oil, there is a decrease in LPG/gasoline, which is consistent with the higher aromatic content of the mixed plastic waste oil accumulating in the gasoline product fraction.

Producing green fuels using FCC

Deriving fuels from biomass replaces fossil carbon with renewable carbon that will not add to the issue of atmospheric carbon accumulation and climate change. Biomass is a broad term referring to a wide variety of plant-derived materials. However, for this discussion, we can narrow our

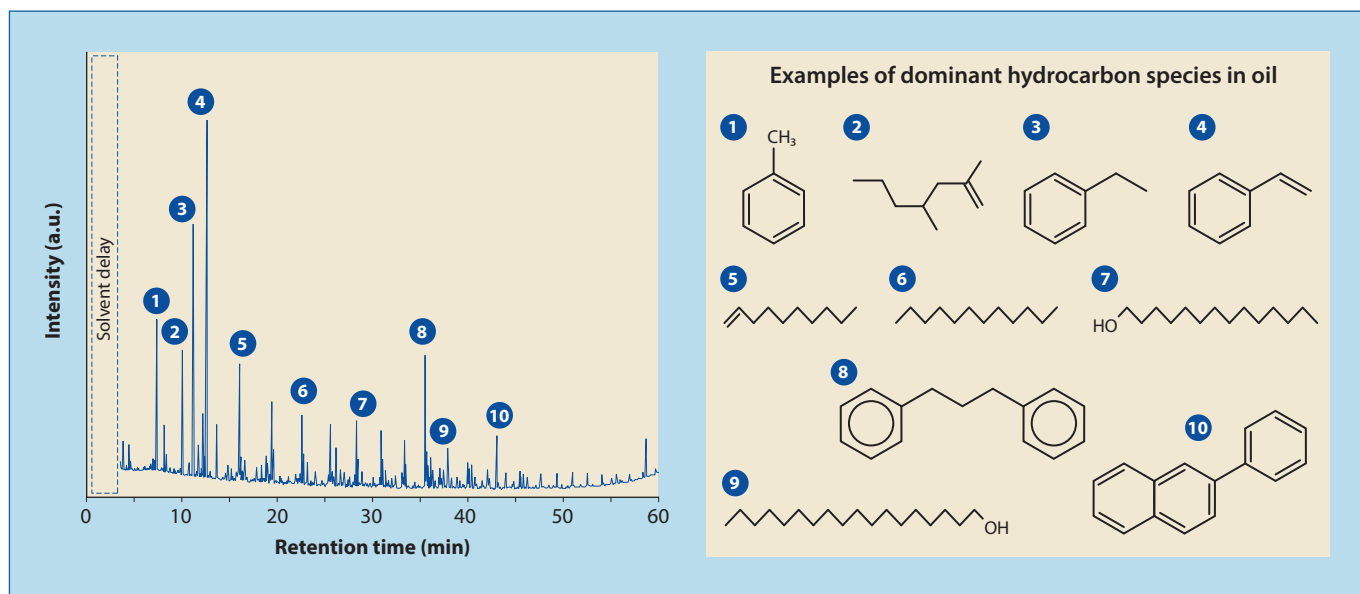


Figure 6 Composition of pyrolysis oil derived from mixed plastic waste with illustrations of dominant species identified using GC-MS

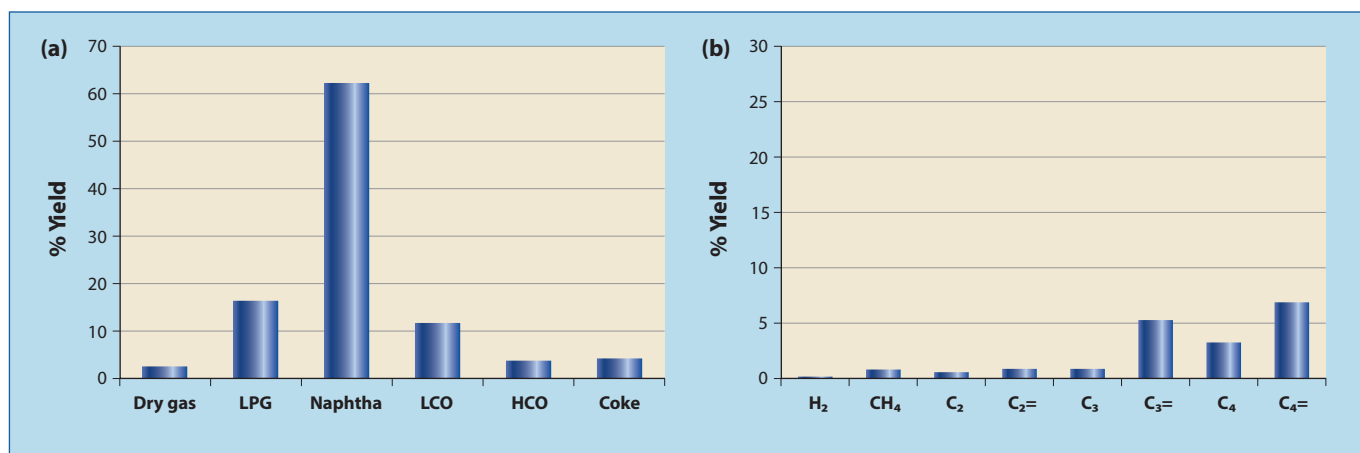


Figure 7 Results from catalytic cracking pyrolysis oil derived from mixed plastic waste using max naphtha catalyst design shown as (a) overall yields and (b) breakdown of dry gas and LPG

focus to biomass solids, such as woody biomass or agricultural wastes, and oils extracted from plants such as vegetable oils. Both sources of biomass offer the potential to incorporate renewable carbon, but their chemistry will be quite different.

Plant-based oils such as corn oil and soybean oil are extracted directly from the plant and consist of a mixture of triglycerides, which are large molecules comprised of glycerol binding together three long-chain fatty acids. Different plant oils will contain different mixtures of triglycerides, but all plant oils will contain long-chain fatty acids with an overall carbon number on the order of 50.³ In general, the distribution of different molecules in plant-based oils will be extremely narrow compared to oils derived from solid biomass via pyrolysis or liquefaction. Further, while there are many different plant oils, they will all be similar in that they are comprised of a relatively short list of different triglycerides and, therefore, will behave similarly as a refinery feedstock. In Figure 2, the effective hydrogen index is lower than conventional gasoil due to the oxygen content. However, the combination of the nature of the glycerol backbone and the highly saturated fatty acids results in a very low concarbon associated with plant oils.

While maybe not commercially practical, it is technically possible to feed these oils undiluted into an FCC unit. This was demonstrated in an experiment conducted in an ACE reactor comparing yields from the incremental replacement of gasoil with soybean oil using the max naphtha catalyst design. **Figure 8** summarises the yields where the conversion is held constant. As the content of soybean oil increases in the feed oil, the yield of LPG hydrocarbons decreases due to structural differences between the gasoil hydrocarbons and the triglycerides. Similarly, the yield of light cycle oil (LCO) increases, which results from an accumulation of less reactive fatty acid remnants. What is absent from the hydrocarbon products is the presence of oxygenates. All of the oxygen contained in the triglyceride is removed through various deoxygenation pathways to produce either water, carbon dioxide, or carbon monoxide. One key takeaway from this experiment is that deoxygenation is inevitable, which will largely be the case for all biomass-derived oils. While deoxygenation cannot be prevented, the design of

the catalyst may allow directing the deoxygenation towards the production of water to preserve renewable carbon or towards carbon oxides to preserve hydrogen.

Oils derived from biomass solids will be significantly more complex. While there are many possible sources of biomass wastes, they are all similar in that they are made up of the same three basic solid structural components: cellulose, hemicellulose, and lignin. What will vary between sources of biomass is the relative amounts of each component, where woody biomass will have higher lignin content than non-woody biomass such as grasses.

The composition of the oil resulting from the pyrolysis of biomass will be the result of the pyrolysis of these three structural components, yielding a molecularly diverse oil comprised of hundreds of oxygenated hydrocarbons. Cellulose and hemicellulose are similar in that they are both polysaccharides comprised of repeating sugar units that, during pyrolysis, yield a broad mixture of small carbonyl and furan/pyran ring compounds. The structure of lignin is quite different, consisting of a complex organic polymer made by cross-linking phenolic precursors. During pyrolysis, lignin will decompose into a mixture of phenols and guaiacols.⁴

Biomass pyrolysis oils will be rich in oxygen and deficient in hydrogen, which together results in the very low effective hydrogen index shown in Figure 2. This, combined with the nature of oxygenated hydrocarbons, results in a high tendency to condense to coke during thermochemical conversion processes, which is reflected in the very high concarbon in Figure 2. The high tendency for coke formation will exceed what a conventional FCC unit can manage, and co-processing with gasoil will be required.

Co-processing with gasoil will both reduce the blended concarbon and provide much-needed in-situ hydrogen on the catalyst surface. The amount of bio-oil that can be processed with gasoil will be dictated by where each feedstock falls in Figure 2. The more hydrotreated and deoxygenated the bio-oil, the higher the concentration of bio-oil that can be co-processed. However, this comes at the disadvantage of higher bio-oil costs.

Co-processing bio-oil with gasoil was demonstrated in an ACE reactor using a pyrolysis oil prepared by Neoliq using waste from olive processing as the biomass source.⁵ The

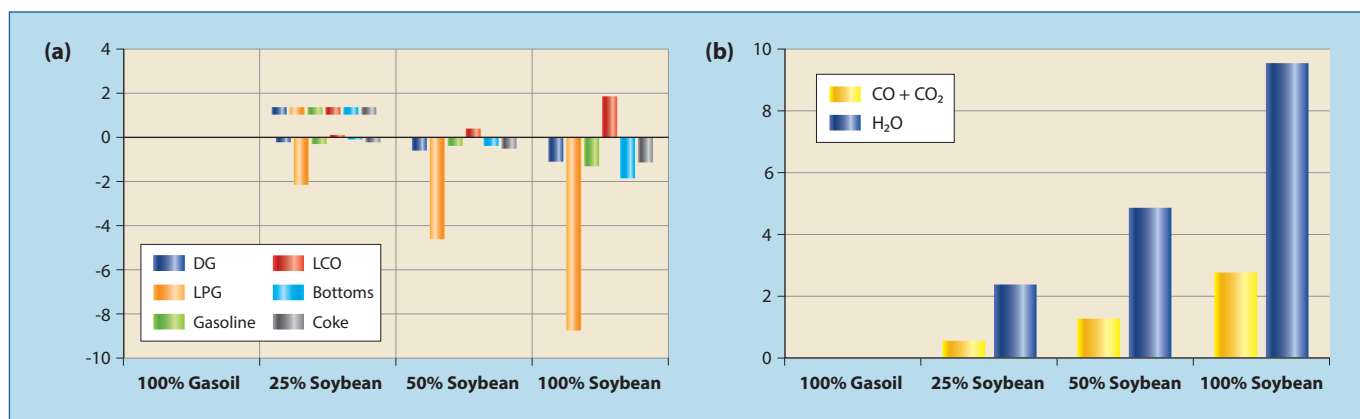


Figure 8 Product yields from catalytic cracking of soybean oil using max naphtha catalyst design shown as (a) overall hydrocarbon yields and (b) yields of deoxygenation products

Characteristics of conventional gasoil compared to select pyrolysis oils

Pyrolysis feedstock	Typical conventional gasoil	Pure LDPE	Mixed plastic waste	Soybean oil	Olive waste
Conradson Carbon Residue API @ 60°F	~0.4%	0.02%	3.9%	0.5%	19.4%
Effective hydrogen index	~24	44	34	22	-5.4
Oxygen content	~1.7	1.9	1.6	1.6	0.6
	0%	0%	3.6%	9.5%	24.0%
Hydrocarbon species					
Aliphatic	~68%	100%	31%	---	0%
Aromatic	~32%	0%	55%	100%	1%
Oxygenated aliphatic	0%		14%	---	9%
Oxygenated aromatic	0%		0%	---	90%

Table 1

properties of this oil relative to the other examples discussed prior are illustrated in **Table 1**. The high oxygen content of the bio-oil was measured to be 24 wt%, which results in a very low effective hydrogen index of ~0.6.

Analysis of the bio-oil using GC combined with mass spectroscopy revealed a significant fraction of the expected mono- and di-aromatics consistent with lignin pyrolysis, consistent with the relatively high concarbon of ~20 wt%. Given its properties, the bio-oil had to be diluted in gasoil at a ratio of 10% bio-oil to 90% gasoil. Even at this relatively low level, the addition of the bio-oil resulted in the coke yield increasing. Additionally, the gasoline yield increased at the expense of LPG and HCO, likely due to aromatics from the bio-oil accumulating in the gasoline product fraction.

Conclusion

Today, we need to improve the sustainability of our existing refinery operations and create new approaches to recycling materials or using renewable feedstocks. Developing these approaches to reduce the amount of fossil carbon extracted from petroleum reserves for the new production of transportation fuels and chemical feedstocks will become an increasingly important topic. This will likely be achieved by both recycling fossil carbon through chemical recycling processes and inserting renewable carbon-based feedstocks into manufacturing processes. For more than 80 years, FCC has been used to convert low-value heavy fractions of crude oil into

higher-value transportation fuels and chemical feedstock. For upgrading challenging, sustainable feedstocks, the flexibility and low cost of FCC may again offer advantages.

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