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# BIO-GASOLINE FROM JATROPHA OIL: NEW APPLICATIONS FOR THE FCC-PROCESS

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## ABSTRACT

*Jatropha curcas L.* is a very drought-resistant plant, and jatropha oil can be extracted from its seeds. Whilst not suitable for human consumption, we found that it is a promising feedstock for producing (bio)-gasoline. The oil was cracked in an internally circulating FCC-reactor using a Grace Davison Ultima® catalyst. The total conversion was around 65%, with ca. 40% gasoline and ca. 25% crack gas (exact numbers varied with reactor temperature). The gasoline has a RON > 95 and oxygen < 0.3% m. The crack-gas consisted of ca. 35% propylene, ca. 13% 1-butene and ca. 6% ethylene.

## THE FEEDSTOCK

*Jatropha curcas L.* (JCL) belongs to the family Euphorbiaceae. *Jatropha* originated in Mexico, Central America and northern South America, but today it grows in many tropical and subtropical countries. In 2008, the worldwide area under cultivation was 900,000 hectares, with Asia (85%), Africa (13%) and South America (2%) being the main producing areas. Estimations suggest that the area of cultivation will increase to a total of 13,000,000 hectares by 2015 (1).

## The Plant

*Jatropha curcas* grows as small tree or bush, with a maximum height of 5-7 m. Its life expectancy is 50 years and the crop yield increases with age. Under normal conditions jatropha seeds are only harvested once a year, but when watered sufficiently or when grown in humid regions, the fruits ripen throughout the entire year (2). As JCL is a tropical to semi-arid climate well-adapted succulent, it can survive three consecutive years of drought by dropping its leaves (3).

*Jatropha* plants grown from seed develop a strong tap root (up to 5 m long) that can help stabilize the soil and prevent landslides. If propagated vegetatively by cuttings, JCL forms a dense root carpet that can prevent erosion and accumulate humus (4).

*Jatropha curcas* grows on a wide variety of soils, except clay-rich soil. Accordingly, well-drained sandy soils with good aeration are preferred (5). *Jatropha* has very low nutrient requirements, but for optimal crop yield fertilization is necessary (6).

Because its leaves are inedible to animals, jatropha is often used as a hedge plant to protect fields from animals. Because of a greater interest in non-fossil sources for fuel, there is an increase in large-scale plantations (1).

## The Oil

The most valuable product of JCL is jatropha oil. The quantity of seeds harvested, the oil content in the seeds and thus the total oil yield vary greatly with the climatic region and cultivation conditions. With optimal watering conditions (ca. 1200 mm precipitation per year) and a high soil fertility of around 6000 kg/ha/a, seed can be harvested (7).

There are two main ways to obtain the oil: mechanical and solvent extraction. Up to 60% of the total oil can be obtained by using a manually operated oil press. If the press is motorized, jatropha seeds can yield up to 75% oil (8). A more efficient way of obtaining the oil is solvent extraction: when using organic solvents (hexane is most frequently used) practically 100% can be extracted, whereas with water-based solvents these values vary from 65% to 100% (depending on temperature and pH-value, amongst others). Since solvent extraction is energetically more demanding, it is only economically practical on a larger scale (4).

Jatropha oil mainly consists of fatty acids. We determined the exact composition by transesterification followed by GC-analysis (according to EN ISO 5509:2000). The oil was found to contain high amounts of unsaturated fatty acids (76.8%) and 23.2% saturated fatty acids. The details are shown in Figure 1.

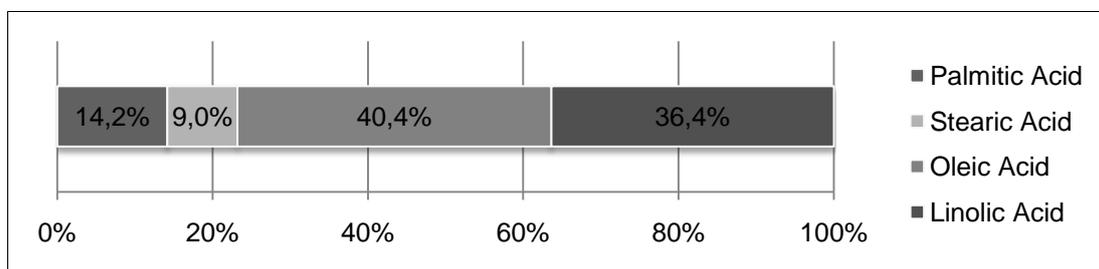


Figure 1: Fatty acid composition of the jatropha oil analyzed

Jatropha oil is unsuitable for human consumption as it contains relatively high amounts of phorbolic esters and lecithins (2). Therefore, unlike conventional biofuel feedstocks (i.e. corn or palm oil), it is not part of the food vs. fuel dilemma.

## EXPERIMENTAL SETUP

### The Pilot Plant

A continuously working fluid catalytic cracking (FCC)-pilot plant (see Figure 2) was used for the experiments. The different areas in the plant consist of the *feed pre-heater*, the *riser* (where the catalyst comes into contact with the feed and where the cracking takes place), the *regenerator* (where the spent catalyst is regenerated) and the *product gas condensation area*. All sections are kept under an inert gas atmosphere (nitrogen), except for the regenerator (this needs oxygen to burn off the coke) (9).

The plant has an internal circulating design, thus the riser is inside the regenerator. This is a major difference from most other FCC-plants, which have external circulation. The main advantages of internal vs. external circulation are:

- compact design
- simplified architecture (i.e. no slide valve for catalyst recirculation or cyclones needed)
- desired heat coupling regenerator (exothermic combustion of coke) – riser (endothermic crack-reaction)

The feed pre-heater is an electrically heated tubular oven. The oil is heated to 300°C. The length of the oven (9 m) helps to level out any peaks in flow rate and thus assures a constant transport of the feed into the reactor.

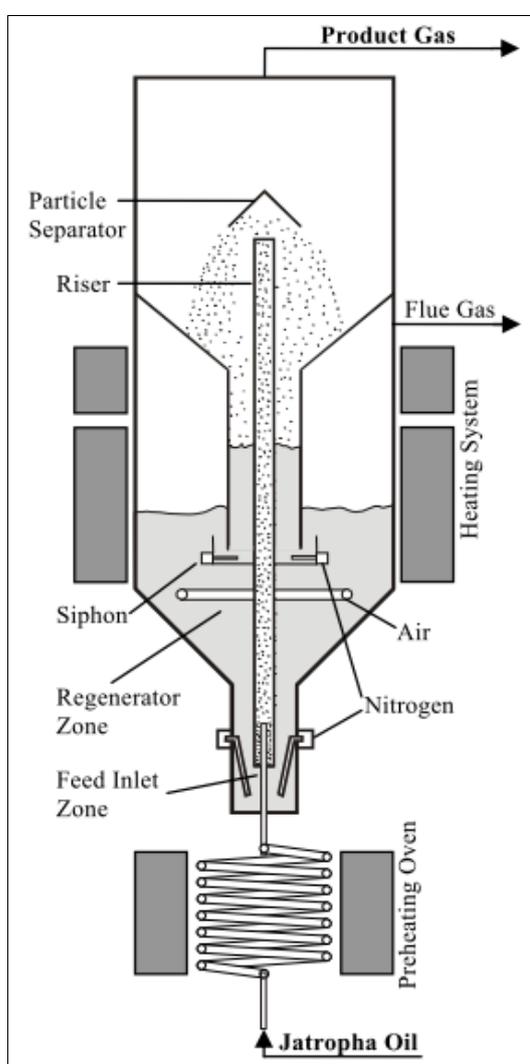


Figure 2: Schematic of the used FCC pilot plant

Inside the reactor, the pre-heated oil comes into contact with the hot catalyst. This leads to vaporization of the oil. The gaseous feed-molecules can then react with the catalyst particles. The cracking reactions produce many gaseous molecules, which in turn are responsible for the increase in volume. This effect causes an upward movement inside the riser. The flow created conveys the catalyst upwards to the particle separator that diverts the catalyst-flow to the regenerator. The product gas, on the other hand, leaves the reactor and is transported to the product gas condensation area, from where samples are taken for analysis.

The spent catalyst circulates internally to the regenerator. Since this area of the reactor is fluidized with air, a siphon (fluidized with nitrogen) is used to strip the catalyst and prevent the air from entering the product gas side. The siphon also enables us to measure the catalyst circulation rate: when the siphon fluidization is turned off, no further spent catalyst can enter the regenerator. As some of the catalyst is still being transported through the riser, the level of catalyst in the regenerator drops. This is measured as a drop in pressure, which is converted into the catalyst circulation rate.

The regenerator is a stationary fluidized bed. Air is used as a fluidizing agent in order to burn off the coke that becomes deposited on the catalyst during the cracking reaction. The average residence time in the regenerator is around 10 minutes.

The bottom section is also built with a fluidization system. Like the siphon, this is used to strip the catalyst coming in from the regenerator and to prevent the catalyst flow from stopping.

### The Catalyst

A standard zeolite FCC-catalyst was used for cracking of the oil. The catalyst was an equilibrium catalyst (e-cat) by Grace Davison (E-Ultima®). For more details, please see Table 1 below.

Table 1: Specifications of the catalyst used

<b>Name of catalyst</b>	Grace Davison E-Ultima®
<b>Type of catalyst</b>	shape-selective zeolite
<b>Particle size range</b>	20 – 200 µm
<b>Mean particle size</b>	75 µm

### ANALYSIS

There were three main components that needed to be analyzed: the flue gas, the gaseous product and the liquid product. Figure 3 shows a schematic of the sampling and analytics.

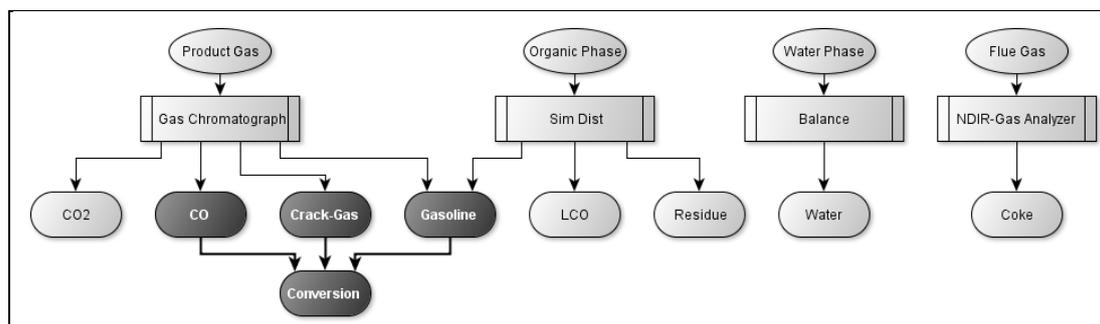


Figure 3: Schematic of the sampling and analytics and assignment to the product lumps

A side-stream of the product gas was sucked away for 15 minutes. The hot gas was run through coolers (first and second stage at 4°C and a third cooler at -20°C) and partially condensed. The still gaseous fraction was collected in a gas-sampling bulb and analyzed immediately. The liquid fraction was stored in a glass bottle for subsequent phase separation.

### Gaseous Phase

The gaseous phase mainly contained crack gas: olefins (propylene, 1-butene and ethylene) and paraffins (linear and iso-paraffins). Another part contained uncondensed paraffins (mainly C<sub>5</sub> and C<sub>6</sub>). This group was added to the gasoline lump (see Figure 3).

Other components in the gas were CO and CO<sub>2</sub>, both of which are only formed in the presence of oxygen contained in the biomass.

## Liquid Phase

The liquid phase was separated into an aqueous and an organic phase. The water formed contained most of the oxygen from the biomass. The rest was found as CO or CO<sub>2</sub> (see the section above). This left the organic phase (gasoline, LCO and residue) practically free from oxygen compounds (total oxygen < 0.3% m.).

The resulting boiling range of the organic phase was measured by a SimDist so that the contents of the gasoline in the product could be determined.

## Flue Gas

The flue gas provides information about the coke formed during cracking. It was analyzed online with two Rosemount® NDIR-gas analyzers. The detected components were CO, CO<sub>2</sub> and O<sub>2</sub>. The amount and composition of the coke formed was determined from this data.

## RESULTS

First, experiments with varying riser temperatures were conducted. Each data point is an averaged from three single values in order to improve statistical significance.

Figure 4 shows the influence of varying riser temperature (averaged along the height of the riser) on the valuable products of gasoline, crack gas and CO. The total fuel yield (TFY) shown was defined as shown in (1) below:

$$TFY [\%] = \frac{m_{gasoline} + m_{gas}}{m_{feed}} \cdot 100 \quad (1)$$

With increasing temperature in the reactor, there was a tendency for smaller molecules to form in the cracking process; this led to an increased production of gasoline (+3% / 100 K) and gas (+9% / 100 K). This was mainly at the expense of light cycle oil (LCO) and residue (-11% / 100 K), and coke, to a lesser extent (-2% / 100 K) (see Figure 5).

The formation of the oxygen-containing products CO (in Figure 4), CO<sub>2</sub> and H<sub>2</sub>O (both in Figure 5) was barely influenced by the increasing average riser temperature. There was no change in CO<sub>2</sub> yield or a redistribution between CO (-1% / 100 K) and water (+1% / 100 K).

Further experiments were carried out in order to compare jatropha oil with vacuum gas oil (VGO, the regular feed for FCC units). These were performed at a mean riser temperature of 550°C, which corresponds to the average FCC operating conditions in refineries.

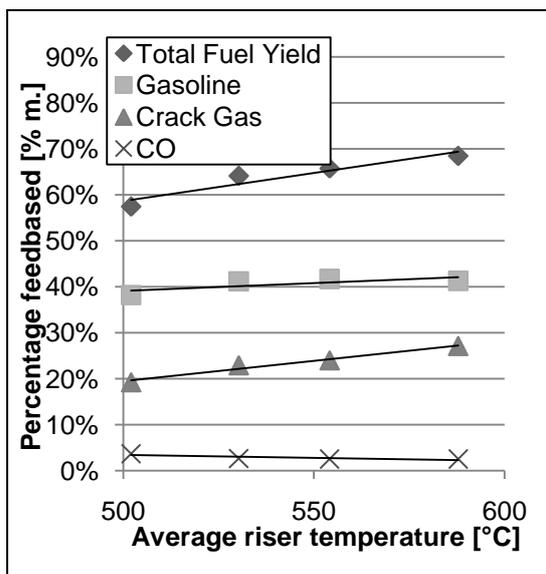


Figure 4: Influence of riser temperature on the formation of gasoline, crack gas and CO

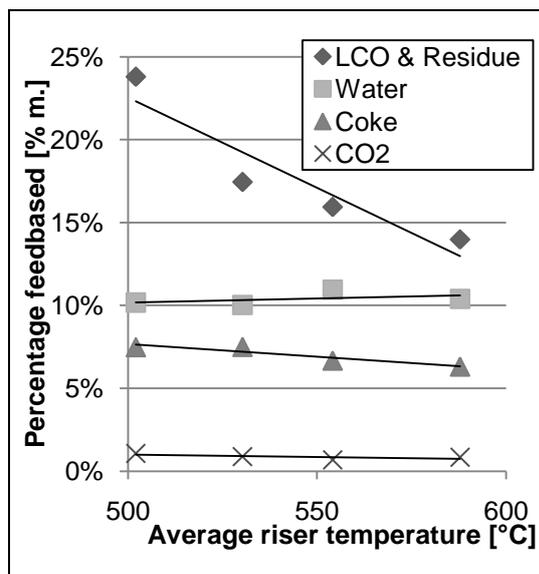


Figure 5: Influence of riser temperature on the formation of LCO & residue, water, coke and CO<sub>2</sub>

Figure 6 shows the products of jatropha oil compared to VGO when used as feedstock. Jatropha oil yielded less gasoline (-9%) and crack gas (-6%) per kilogram feed than vacuum gas oil. This was mainly due to the formation of water (+11%) and CO<sub>2</sub> (+1%). The oxygen contained in the triglyceride converted into these components.

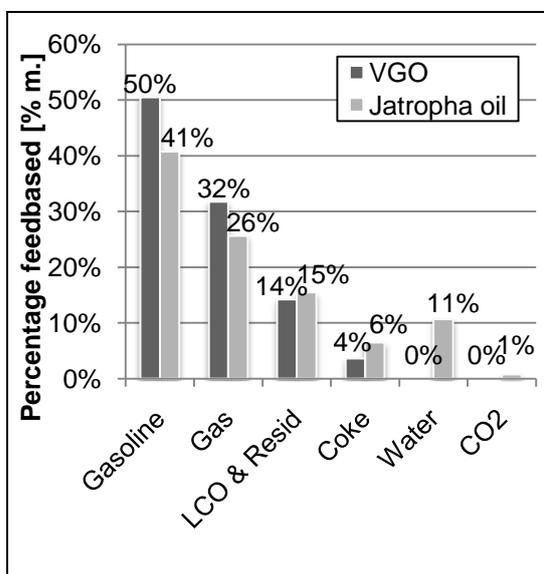


Figure 6: Products lumps of jatropha oil as feed compared to VGO (at 550°C riser temperature)

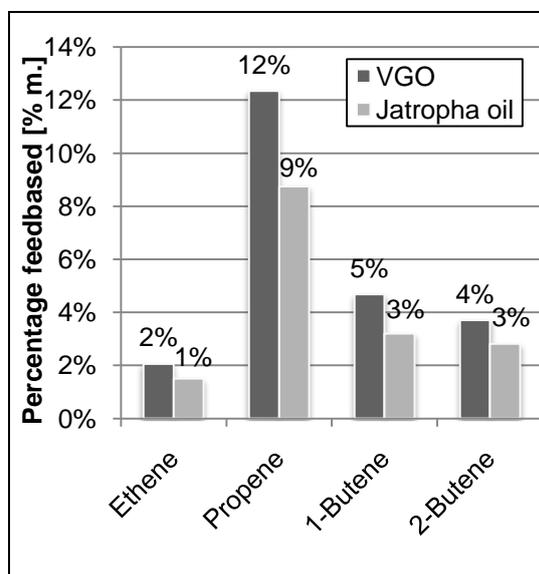


Figure 7: Olefins contained in the crack gas of jatropha oil as feed compared to VGO (at 550°C)

Figure 7 depicts the olefin contents of the crack gas. Compared to VGO, the jatropha oil showed a similar distribution of the olefins. The composition of crack gas was about the same for both feeds. The decrease shown above was due to the aforementioned formation of water (and the subsequent reduction in gas yields).

Figure 8 shows the results of a PIONA analysis: paraffins, iso-paraffins, olefins, naphthenes and aromatics. It was performed using two-dimensional GC-analysis (GC x GC).

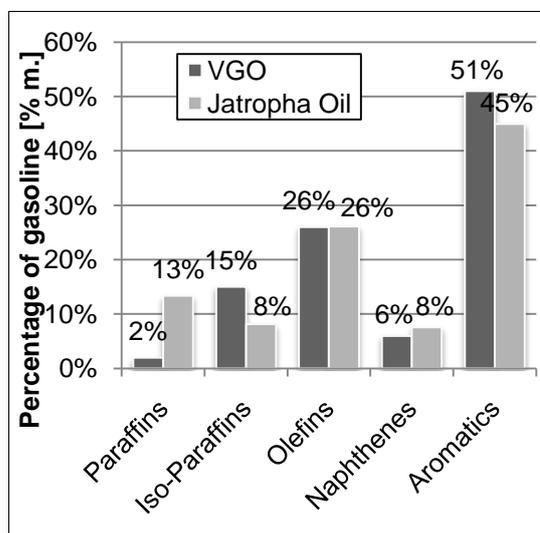


Figure 8: PIONA results of gasoline produced

Jatropha oil produced fewer aromatics (-6%) and iso-paraffins (-7%). The increase in paraffins (+11%) and naphthenes (+2%) compensated for this.

Table 2 compares the gasoline properties with the current legal specifications. The research octane number (RON) and the motor octane number (MON) were comparable to regular FCC gasoline (from VGO). This was mainly due to the very high amounts of aromatics and i-paraffins still present.

The gasoline from the jatropha oil contained virtually no lead. The sulfur contents was also considerably lower

than with regular FCC gasoline from VGO. As mentioned before, almost all of the oxygen contained in the biomass was removed: only 0.3% was found in the liquid product.

Table 2: Comparison of gasoline properties with current legal specifications

Property	Unit	Legal min	Legal max	Jatropha gasoline	Common FCC-gasoline
RON	-	95		95	91 – 96
MON	-	85		81	78 – 84
Density	kg/m <sup>3</sup>	720.0	775.0	801.1	
Pb-contents	mg/L		5	< 0.1	
S-contents	mg/kg		10	2	100 – 2000
O-contents	% m.		2.7	0.3	

## ACKNOWLEDGEMENT

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## NOTATION

CO	Carbon monoxide
FCC	Fluid catalytic cracking
GC	Gas chromatography
JCL	<i>Jatropha curcas L.</i> , botanical name of the jatropha plant
LCO	Light cycle oil
MON	Motor octane number
PIONA	Acronym for paraffins, iso-paraffins, olefins, naphthenes, aromatics
RON	Research octane number
TFY	Total fuel yield
VGO	Vacuum gas oil

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