

SYNTHETIC CRUDE OIL FROM PETROLEUM WASTE MATERIALS

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Introduction

As the demand for petroleum and petrochemical products is steadily increasing, there is also an increase of petroleum derived wastes and residues from crude processing. These materials are considered to be an environmental problem of increasing significance, as further utilisation will become more and more difficult due to restrictive emission limitations in most countries.

The VEBA-COMBI-Cracking (VCC) process is capable to convert a.m. materials. It is a hydrogen addition technology, which directly combines liquid phase hydrogenation with an integrated catalytic hydrofinishing step. The process had been developed and commercially applied for coal liquefaction and for conversion of residual oils as well as for upgrading of heavy crudes. Two licences have been granted, one for upgrading Canadian tar sand derived bitumens and the other to a refinery for crude processing without heavy fuel oil production. Its most recent application is given by its plastic to oil operation. The capability to convert mixed waste plastics into chlorine free oil, enables industry to perform a close recycling loop for plastics on a new material base.

The Basics of the Hydrogenation Process

The main objective of the hydrogenation is to convert organic materials like coal, vacuum residues or difficult to handle organic wastes like chlorine contaminated solvents, used tubes, PCB's or particularly mixed plastic wastes into valuable clean hydrocarbon products.

Liquid phase hydrogenation takes place at temperatures between 450 °C and 490°C and hydrogen partial pressures of 150 to 250 bar. Under these conditions large molecules are cracked and hydrogen is added to the cracked organic bonds. Sulfur, nitrogen and chlorine after being separated are transferred to their corresponding hydrogen containing components which can be recovered.

The cracking process starts at the weak bonds of the molecules. The bond strength is decreasing from carbon/carbon over sulfur/carbon and nitrogen/carbon to chlorine/carbon bonds. The decontamination of used solvents and other chlorinated organic wastes like mixed plastic wastes take advantage of this fact, as shown in Figure 1 for e.g. for trichloroethane, trichlorobenzene and PCB's. Basically the chlorine is converted into HCl and neutralised *in situ* by the addition of a caustic material forming an inorganic salt.

The VEBA COMBI Cracking Technology

The VCC technology is a thermal hydrocracking/hydrotreating process for conversion of petroleum residues at high conversion rates (>85%, 624°C+). A simplified flow scheme of the VCC process is shown in Figure 2.

The feedstock is started with a small amount of coal derived additive, which is added to suppress coke formation at elevated temperature. After being fed into the high pressure section, which is operated at a pressure level between 150 bar and 250 bar, the slurry is mixed with make up hydrogen and recycle gas. This mixture is preheated and routed to the liquid phase hydrogenation (LPH) step for primary conversion. The LPH reactors are operated in a temperature range between 440°C and 460 °C. Temperature is controlled by a cold gas quench system.

The LPH products are routed to the hot separator (HS), where gases and vapourised products are separated from the nonconvertibles. Distillates in the HS bottoms are recovered by a vacuum flash. The bottom product leaving the flash tower is the hydrogenation residue, which includes the additive.

The HS overheads, together with the recovered HS distillates are the feedstock for the integrated gas phase hydrogenation (GPH) step which is operated at same pressure level as LPH. To adapt the product slate to seasonal demands straight run distillates can be treated additionally in the GPH step. The temperature of the catalytic fixed bed reactors are adjusted with respect to the required product qualities. Typical temperatures are in the range between 340°C and 380 °C (SOR). Temperature control is performed by an hydrogen quench.

The separation of the synthetic crude oil and the hydrocarbon carbon gases is performed in the cold separator. The Syn crude is depressurised and sent to a stabiliser and fractionation column, where as the gases are routed to a scrubber. Part of the gases after passing a lean oil wash are fed back as recycle gas to the feed of the LPH section.

Processing of Plastic Wastes

Plastic wastes need special attention with regard to its feeding to high pressure processes like the VCC process. One option is to grind the plastics down to particle sizes below 1 mm, slurry it with petroleum residue and pump the slurry into the process. The disadvantages of this procedure are the high costs for grinding and the limitation of the plastic/oil ratio to below 10 % due to viscosity restrictions.

The other option is to depolymerize the plastics to a certain degree by applying elevated temperature and then pump the liquefied material to the hydrogenation process. This enables a significantly higher plastic/oil ratio and decreases the amount of chlorine which has to be neutralized in the hydrogenation process. The plastic wastes are split into four fractions: gas, hydrochloric acid, condensates and depolymerizates containing the Inerts. Figure 3 shows the result of plant operation. A simplified process scheme of the depolymerisation unit is shown in Figure 4.

The VCC Demonstration Plant

The demonstration plant has been constructed and operated to demonstrate the improved Bangius-Pier technology for hard coal liquefaction from 1981 to 1987. In parallel the basic test runs for development of the high conversion mode of residual oils in VCC had been run in small pilot plants and a large pilot plant. Figure 5 shows the feedstocks processed and Figure 6 indicates the feedstock quality ranges covered. The data basis generated by these test works made it possible to transfer this technology into commercial scale.

In 1987 the demonstration plant was modified to enable petroleum residue conversion with a capacity of 24 t/h. Yield structure and the achieved product qualities are given in Figure 7 and Figure 8. After successful operation with residues from crude distillation and visbreaker operation an increasing share of the residues were substituted by a. m. chlorine containing wastes.

In October 1993 a depolymerisation unit with a design capacity of 5 t/h was erected at site of the demonstration plant to liquify the plastics. Together with the vacuum residue the liquid products of the depolymerisation step are fed to the VCC unit. In Figure 8 the qualities of the VCC syncrude derived from the coprocessing of vacuum residue and plastic wastes are compared to those of the straight run products of Arabian Light, indicating the high quality standard of the VCC products.

According to new developments in PDU tests the process of plastics depolymerization can be triggered in such way, that app. 70 wt % of the plastics are converted into light condensates and only 20 wt % will leave the process as heavy depolymerizates. This enhanced mode of operation offers a new and very economic sound possibility of processing depolymerisation products. As the condensates do not contain any solids, only mild hydrotreating needs to be applied for removal of the organic bound chlorine.

The enhanced mode of operation will be applied to the demonstration plant after having integrated an hydrotreater unit for separate processing of the condensates. Then only the heavy depolymerizates have to be fed to the VCC unit. A simplified flow scheme of this operation is given in Figure 10. According to this mode of operation it is possible to increase the capacity for plastic conversion from app. 40 000 t/y up to 120 000 t/y.

Large scale VCC-plant connected to a refinery including waste processing

As mentioned above, for VCC operation the plastic wastes are hydrogenated commingled with crude oil residue. Part of the syncrude produced needs further treatment, be it in a reformer (gasoline) or a cracker (vacuum gasoline). It is therefore very advantageous to have the upgrader closely connected to a refinery, which can also supply energy and water and can take over the waste streams. Such an arrangement is shown in Figure 11.

For a plant with a total conversion capacity of 1.35 Mio t/a year, the relevant input and output streams are listed in Figure 12. The investment costs for such a plant have been estimated based on an extended basic engineering and on quotes for all larger pieces of equipment. The estimate for the investment is as high as 1,020 Mio DM (1993 basis).

Assuming today's market prices for syncrude, vacuum residue, energy etc. the plastic wastes have to pay a "gate-fee" of roughly 200 DM/t in order to keep the operation profitable according to refinery standards.

Another example is given for the processing of chlorine containing waste materials. A plant capacity of 25 000 BPSD has been chosen, out of which one-third is used for waste materials.

Value of waste materials (free upgrader plant in Germany)

- Used tube oils	3/t	approx. 0
- Materials ≤ 0,2 Chlorine	3/t	approx. 200-250
- Pure PCBs	3/t	approx. 1500-1800

For the purpose of this evaluation an average credit of 300 3/t is assumed. Operating expenses are nearly covered by the value of the syncrude produced from processing these materials.

- Savings	MMS/year
- 8330 BPD vacuum resid ¹⁾	27
- Credits ²⁾ from waste processing	110
	<u>~ 130 - 140</u>

1) at 10 \$/BBL (HFO)

2) density 1.2 [g/ml]

This example illustrates drastically the high profitability of processing those materials at least under the conditions prevailing in Germany. These high credits can buffer almost any swing in crude/HFO prices.

Summary

Feedstock recycling of post consumer plastics is reality also in commercial terms. The main advantages of the depolymerisation/hydrogenation process are

- no sorting in different kinds of plastic is necessary
- high liquid yields
- high quality chlorine free syncrude which enables its use in existing refineries without restrictions
- no feedstock related pollution

The cost estimation for a large scale unit had shown that feedstock recycling by hydrogenation is very well competitive to alternative processes and may well compete with thermal utilisation if stringent environmental restrictions have to be taken into account.

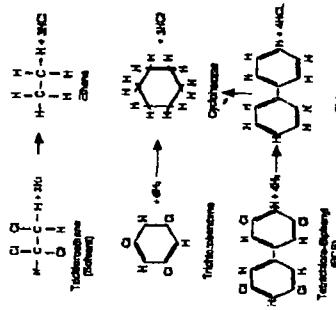


Figure 1: Hydrogenation of Chlorinated Products

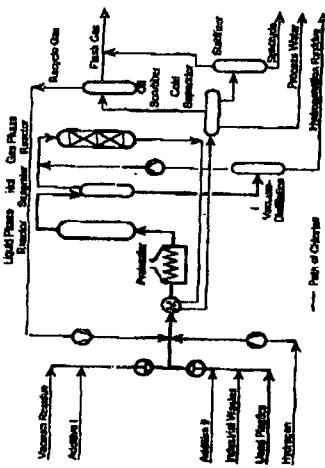


Figure 2: Simplified Process flow Scheme of the YCC Process

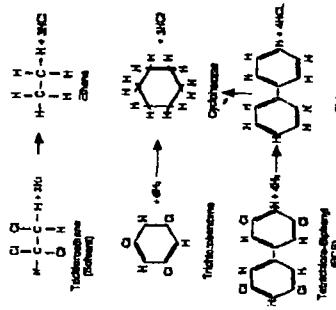


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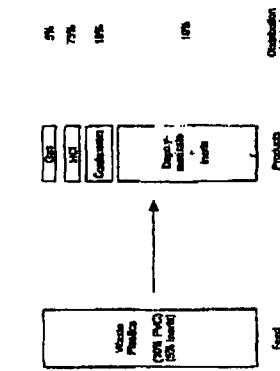


Figure 3: Eigenvector selection

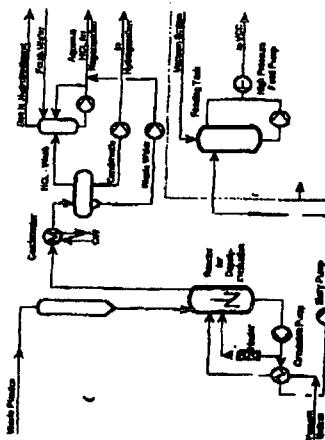


Figure 4: Feeding System for Plastic Yacht

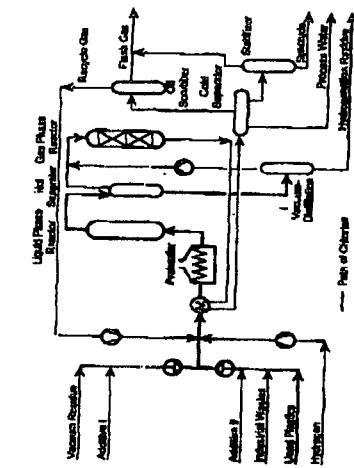


Figure 5: Feedstocks processed up to now

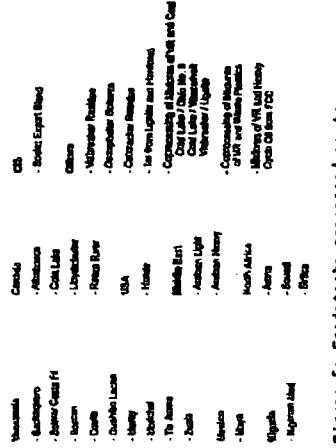
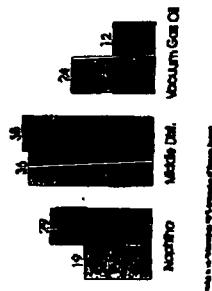


Figure 7: Typical WCC-1101s



		VOC Pre-treatment	Ambient Light Circum. Oil
Grease	-1 - 14		
DishDeter.	0 - 30		
Batter	0.7 - 7.0		
Nitrogen Molecules (V + N)	0.1 - 1.3		
SPM	0.012 - 0.02		
Concentrated Carbon	-12 - 60		
Hydrogen Isobutylene	0.1 - 10		
		Height [cm] (10 ⁻³)	Height [cm] (10 ⁻³)
		Close to T _c	Close to T _c
		6	6
		10	10
		15	15
		ppm	ppm
			Height Deterioration (100 - 300 °C)
			Height [cm]
			6
			10
			15
			ppm

Figure 6: Feedstock Quality Ranges covered

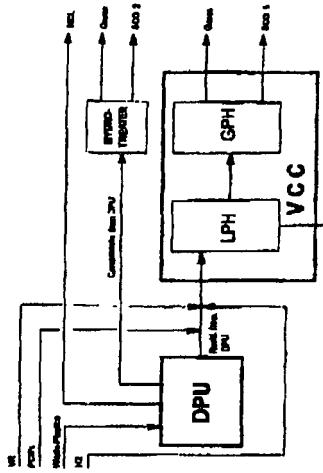


Figure 9: Product Qualities from Plastic Hydrogenation compared to Arabian Light Crude Oil

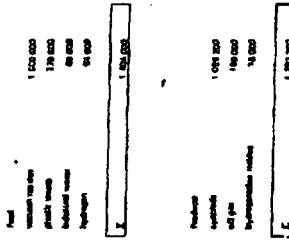


Figure 10: Enhanced Mode of Operation for Plastics/Oil Conversion

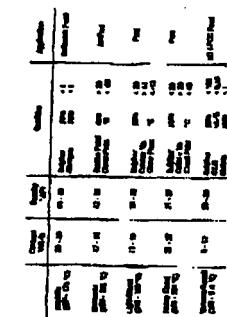


Figure 8: Qualities of the Synthetic

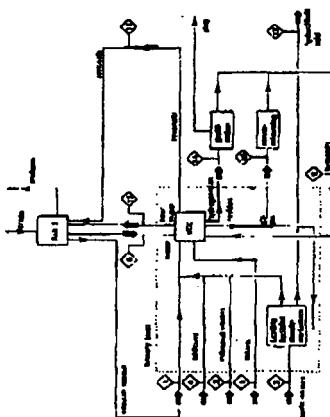


Figure 11: Integration of the WCC-Plant into a Refinery Scheme



Figure 12: Mats Input/Output Data