The VEBA-COMBI-CRACKING-Technology: An update

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Abstract

The main focus on VEBA-COMBI-CRACKING (VCC) during the years 1977 to 1988 has been in the areas of process improvements and extension of the feedstock data base (different crude sources) in smaller scale units as well as testing of new equipment and metallurgical compositions in the Demonstration Plant Bottrop. In summary, this effort has strengthened the VCC design basis which consequently lead to the grant of two licenses, one to the Canadian OSLO group for upgrading of 86000 BPD Athabasca bitumen (1989) and the other to the German OMW-Refinery (Oberrheinische Mineralölwerke, Karlsruhe) for the conversion of 25000 BPD of Arabian Light vacuum resid commingled with FCC slurry oil (1991).

1. INTRODUCTION

Meanwhile other aspects have impacted VEBA OEL's directions for VCC process application in addition to virgin refinery resids and heavy oil upgrading, such as:

- utilizing pretreated refinery by-products such as deasphalter bottoms, FCC slurry oil, visbreaker vacuum bottoms
- coping with the latest transportation-fuel specifications, e.g. low aromatics content in the middle distillate (diesel, light heating fuel oil)
- recycling of waste materials (e.g. used lube oils, chlorinated hydrocarbons, etc.) with the aim of decontamination/refining thereby generating new refinery feedstocks
- utilization of solid waste products such as spent refinery catalyst (e.g. Ni/Mo, Co/Mo hydrotreating catalyst), spent activated carbon.

Specifically the latter two applications which are executed on a day-to-day business in the Demonstration Plant Bottrop, have proven, that the high conversion VCC hydrogenation technology can contribute in an optimum manner to the recycling of environmentally problematic groups of components.

Especially in the latter context, the most recent development yielded into the conversion of unsorted mixed plastics from the household streams into

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refinery feedstocks, allowing a closed production and utilization cycle in an environmental favourable way.

2. THE PRINCIPLES OF THE VEBA-COMBI-CRACKING TECHNOLOGY

The VCC technology is a thermal hydrocracking/hydrogenation process for converting petroleum residues at very high conversion rates (>95%, 524°C+) and liquid yields above 100 vol.% into directly marketable distillates. The process (Fig. 1) applies the principles of the former Bergius–Pier technology for the conversion of heavy residual oils and coal into light distillates. The feedstock is slurried with a finely ground additive, preheated after adding recycle gas and make-up hydrogen and fed into the liquid phase hydrogenation reactors, where the conversion in a once-through mode of operation takes place at temperatures between 440 and 485°C and pressures up to 250 bar. The liquid phase reactors have no internals and are operated in an upflow mode. Temperature control is achieved by cold gas quench.

The unconverted residual oil and the additive are separated from the vaporized reaction products and the recycle gas in a hot separator. The hot separator bottom product is fed into a vacuum flasher for additional distillate recovery. The hot separator overheads combined with the recovered distillates are routed to a directly connected hydrotreating unit (GPH-reactors) operating under essentially the same pressure but at a somewhat lower temperature than the LPH unit. This secondary hydrotreatment/hydrocracking applying a standard fixed bed catalyst produces a high quality synthetic crude oil (SCO) (Table 1). Straight-run distillates, light cycle oil, visbreaker distillates and others may additionally be added to the GPH feed stream.

As the GPH reactors are operating in a pressure range above typical hydrocracking conditions, mild hydrocracking can also be applied, to allow for a shift in yield structure due to seasonal requirements.

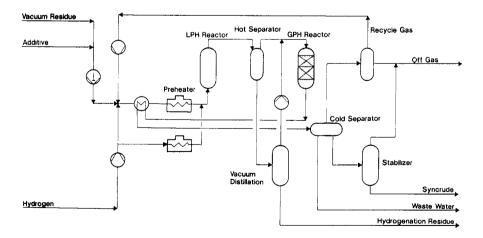


Fig. 1. Simplified VCC process scheme.

After leaving the GPH unit the SCO is cooled, condensed and separated from the recycle gas. The recycle gas after passing through a lean oil washing system is recycled to the LPH unit.

The remaining hydrogenation residue can be used in different areas as illustrated in Fig. 2.

Due to the small amount (\leq 6% related to the feed stream to the primary conversion reactors), gasification may only be applied in high priced natural gas scenarios, in case of a shortage in natural gas or in areas with very stringent environmental restrictions. In these cases, VEBA OEL's proprietary commercial gasification technology may be applied.

TABLE 1

VEBA-COMBI-Cracking typical syncrude properties

	Content (Vol.%)	Density (° API)	Qualities		Application
Naphtha (IBP-350°F)	26-30	64–58	Sulphur, ppm Nitrogen, ppm	< 1 < 1	Reformer feed
Kerosene (350–460°F)	17-21	42–28	Smoke point, mm Cloud point, °C	> 20 < -60	Jet fuel
Light diesel (460–570°F)	15–19	36-32	Sulphur, ppm Cetane No.	< 50 > 45	Pool
			Cloud point, °C	< -15	
Heavy diesel (570-730°F)	23-27	31-27	Sulphur, ppm Cetane No.	< 50 > 50	Pool
			Cloud point, °C	< 40	
Vacuum gasoil (730–950°F)	9–13	29–26	Sulphur, ppm CCR, wt% Metals, ppm	< 100 < 0.15 < 1	HC/FCC Feed

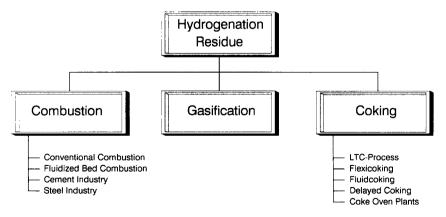


Fig. 2. Hydrogenation residue utilization.

VCC residues are well suited for either conventional combustion or circulating fluidized bed combustion which has been proven in appropriate combustion tests with different vendors.

As a third alternative, coking of the hydrogenation residue by applying VEBA OEL's LTC (Low Temperature Carbonization)-technology leads to further liquid yield improvement and reduction of the "left overs" at low investment costs. The remaining coke of the LTC process is easy to handle and can be used as landfill (if admissible), sold to the cement industry or used for energy generation. If available also other coking processes can be used, utilizing the unconverted VCC bottoms as part of the feed to the coking unit.

Another very attractive area for VCC hydrogenation residue utilization is it's application as a binder in the coke oven industry for the production of blast furnace coke. In this area the residue is replacing traditionally used coal derived pitches for blast furnace coke quality improvement. When the coalderived pitches are high priced, the VCC hydrogenation residue is very much appreciated by coke oven plant operators resulting in a reasonable price for the VCC residue covering at least transportation cost from the upgrader plant to the location of the coke oven plant. Therefore this specific application is preferably recommended.

3. FEEDSTOCK FLEXIBILITY

One of the major advantages of the VCC process is its independence in feedstock quality at high conversion mode of processing. Preferable vacuum residues with cut points above 500°C (932°F) are fed to the liquid phase hydrogenation system (LPH). Neither high Conradson Carbon and asphaltene contents nor high metal contents significantly influence the maximum achievable residue conversion.

Beside virgin vacuum residues also thermal or chemical/physical pretreated bottom streams are possible feedstocks for the LPH. While Visbreaker vacuum residue and Solvent Deasphalter Bottoms can be used as a main source, FCC slurry oil and pyrolysis oil may be used as a supplementary feed if required by the overall refinery material balance. The reactivity of different feeds to the LPH-section of the VCC-process is illustrated in Fig. 3 for some selected feeds. Until now, no feedstock restrictions have been identified.

The processability of Deasphalter Residues as a single feed as well as in mixture with FCC slurry oil has been evaluated in a VCC pilot-scale unit during a test period of several weeks.

An analytical characterization of the feedstocks is given Table 2. The deasphalter residue origins from a ROSE Deasphalter Unit and shows high Conradson Carbon, metals and sulfur contents. Regarding the FCC slurry oil, especially the solids content and the aromatic structure are characteristic.

The residue conversion as a function of LPH reactor temperature is given in Fig. 4. With both, pure Deasphalter Residue feed and Deasphalter Residue commingled with FCC slurry oil, 95% residue conversion has been obtained. The Deasphalter Residue turned out to be a feedstock with a reactivity

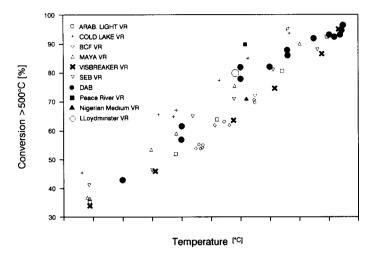


Fig. 3. LPH-Data base. Temperature vs. conversion > 500 °C.

TABLE 2
Feed stock properties of deasphalter bottoms and FCC slurry oil for VCC pilot-scale tests

Property	Deasphalter bottoms	FCC Slurry oil
Density, g/ml	1.076 (20°C)	1.065 (80°C)
Carbon, wt.%	83.30	88.99
Hydrogen. wt.%	9.14	7.22
Sulphur, wt.%	6.30	2.61
Asphaltenes, wt.%	16.8	0.8
CCR, wt.%	29.3	5.2
Solids, wt.%	0.04	1.3
Metals (Ni + V), ppm	323	< 5
IBP, °C	451	212
°C, wt.%	97.5	_

comparable to virgin vacuum residues like Arabian Light and Maya VR. The addition of FCC slurry oil did not influence the residue crackability significantly.

The final bottoms free synthetic crude oil for both feeds (after hydrotreatment in the GPH) is given in Table 3. It is obvious that even with highly aromatic feedstocks, like FCC slurry oil, typical product quality targets e.g. aromatics content and smoke point in jet fuel can be fulfilled.

A more general view on aromatics saturation is given in Fig. 4a for processing Athabasca bitumen at different space velocities and average reactor temperatures at 160 bar H₂ partial pressure applying a standard Ni/Mo hydrofining catalyst. The aromatics concentration in the feedstream (primary syncrude from LPH, hot separator bottoms distillation products, straight runs) was 25 wt% (NMR-analytics) aromatic carbon.

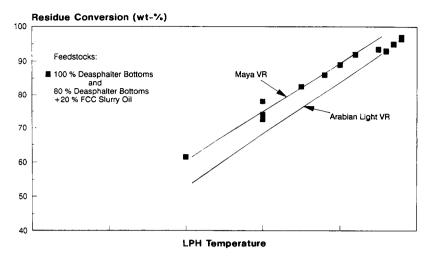


Fig. 4. Reactivity of selected residues.

TABLE 3

VCC Product quality (feedstock: deasphalter bottoms)

Heavy naptha		
Sulphur, ppm	1	
Nitrogen, ppm	2	
Jet fuel		
Sulphur, ppm	< 10	
Aromatics, Vol.%	22	
Freezing point, °C	-46.5	
Smoke point, mm	20.3	
Heavy diesel		
Sulphur, ppm	10	
Cetane index	44	
VGO		
Sulphur, ppm	< 50	
Nitrogen, ppm	< 100	
CCR, wt.%	< 0.1	

Using the typical GPH operation window a degree of aromatics saturation (in total liquid product, TLP), depending on specific conditions can be as high as approx. 75%. The other important information given by this graph is the fact, that even at severe operation conditions, aromatics saturation reaction is still far away from any equilibrium situation which mainly is impacted by the operating pressure. This high operation pressure is the result of the integrated operation of primary conversion and hydrofinishing.

Figure 4b illustrates the impact of the H₂ partial pressure on aromatic saturation at moderate space velocity for Athabasca bitumen and Bachaquero

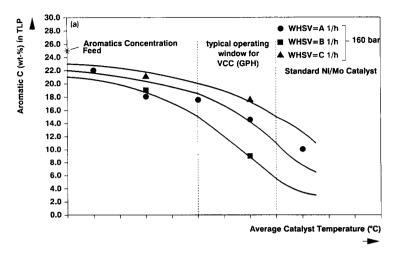


Fig. 4a. Aromatics saturation for Athabasca bitumen as feed as function of GPH-reactor temperature and space velocity.

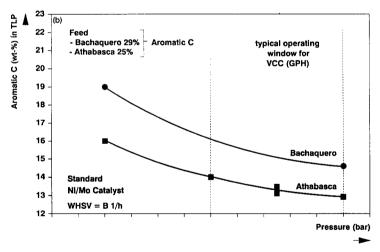


Fig. 4b. Impact of process pressure on the saturation of aromatics in the GPH.

17. The feed quality was 25 resp. 29 wt% aromatic C. The final concentration in TLP was 13 resp. 14 wt% aromatic C. Even starting from different levels of aromatics concentration in the feed, the final result at severe conditions is not that different, but still showing some impact from the feed quality. The advantages of operating on the typical VCC—GPH window are:

- · the high degree of aromatics saturation
- potential for mild hydrocracking operation
- suppression of coke make.

Liquid yields, liquid product distribution and hydrogen consumption data are given in Table 4 for the deasphalter bottoms feedstock. The total liquid

TABLE 4

Liquid yield and hydrogen consumption at 95% residue conversion (feedstock: deasphalter bottoms)

Conversion (> 524 °C), wt%	95	
Liquid yield, vol.%	100.0	
Liquid product distribution		
Light naphtha < 82°C, wt.%	5.8	
Heavy naphtha 82–177°C, wt.%	15.2	
Jet fuel 177–260°C, wt.%	27.5	
Heavy diesel 260-343°C, wt.%	29.5	
VGO > 343 °C, wt.%	22.0	
Hydrogen consumption, Nm^3/t	360	

yield was 100% on a volume basis. The hydrogen consumption amounts to 360 Nm³/t of LPH feed. By varying the operating condition in the GPH unit of the VCC process the liquid product quality and distribution can be adapted to the refiners specifications.

4. THE DEMONSTRATION PLANT BOTTROP

4.1. History and present configuration

The Demonstration Plant Bottrop, also called Coal Liquefaction Plant Bottrop ("Kohleölanlage Bottrop"), was in operation from 1981 until April 1987 for the demonstration of the improved Bergius–Pier Technology for coal liquefaction on a technical scale. The plant has demonstrated its ability to achieve liquid yields > 50 wt%. During a continuous operation of more than 5000 hours the reliability of the technology has also been successfully shown resulting in the demonstration of the commercial readiness of the technology. As this demonstration program ended in April 1987 the plant subsequently has been converted into a residual oil conversion plant as lined out with its outside battery limits connections in Fig. 5.

As can be seen, the RUHR OEL refinery Scholven (a joint venture between VEBA OEL and Petroleos de Venezuela) supplies refinery vacuum resid (virgin vacuum resid as well as visbreaker vacuum resid) for conversion in the Demonstration Plant Bottrop. The produced synthetic crude oil is taken back to the RUHR OEL refinery as well as the offgas. The three connecting pipelines have a length of 15 kilometers each. The necessary hydrogen for the VCC process is supplied by a nearby hydrogen pipeline. The utility interconnection (fuel, steam, water and waste water) is interlinked to a nearby coke oven plant of RUHR KOHLE AG, VEBA OEL's partner in the Demonstration Plant Bottrop. The necessary additive for the process is purchased on the market.

The left-overs of the VCC technology, the hydrogenation residue, is solidified on a stainless steel conveyer belt and transported to the nearby coke oven

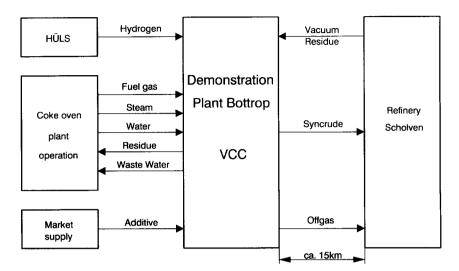


Fig. 5. Demonstration Plant Bottrop. Outside battery limits connections.

plant. The hydrogenation residue is used in this plant for quality improvement of the blast furnace coke produced. By using the existing equipment from the former coal liquefaction time, the Demonstration Plant Bottrop presently has a capacity of 3500 BPD (200000 t per year) vacuum resid. During the operation time from January 1988 until now the plant has demonstrated the reliability of the design data, its easy operability (as can be seen in Fig. 6, the very smooth LPH reactor temperature over time) and high on stream factor ($\geq 90\%$).

For processing of visbreaker vacuum resid Table 5 gives feed and Syncrude overall qualities and yield distribution for a conversion rate above 90 wt%. Table 6 gives a more detailed survey on product cuts. As the syncrude produced is routed into the crude pool of the Scholven refinery and therefore is commingled with other crude fractions, no high quality of the fractions is required, as they are anyhow routed to further processing.

4.2. Recycling of waste materials

Limited irrecoverable resources and environmental protection (e.g. no further landfills) are driving forces for the recycling of waste materials. Hydrogen addition technologies can be an excellent way to chemically decontaminate waste materials by simultaneously producing high valuable refinery products. That is why in addition to processing of refinery vacuum resids of any kind the Bottrop plant has demonstrated during the recent years that it is also able to convert different kinds of waste materials into valuable refinery feedstocks in an environmentally safe manner. The following feedstocks have successfully been processed (commingled with refinery vacuum resids) demonstrating the forgivingness of the technology:

- · used lubricant oils
- · cutting oils

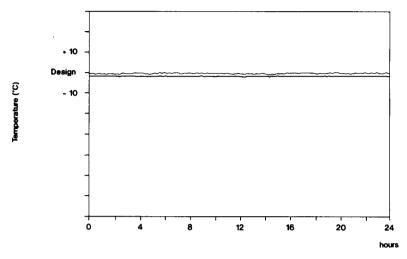


Fig. 6. Temperatures of LPH reactors during stationary operation (VCC Plant Bottrop).

TABLE 5

Typical feed and product qualities for the VCC process (Demonstration Plant Bottrop)

	Feedstock		
	Visbreaker VR	Syncrude	
Ultimate analysis			
C, wt.%	86.1	86.8	
H, wt.%	10.4	13.1	
S, ppm	24000	320	
N, ppm	6000	170	
O, ppm	5000	500	
Density, g/cm ³	1.008	0.844	
Naphtha SB-180°C, wt.%	_	29	
MD 180-370°C, wt.%	_	54	
VGO 370-500 °C, wt.%	18.5	17	
VR > 500 °C, wt.%	81.5	_	

- · residues from degreasing plants
- · chlorinated used solvents
- · painting sludges
- PCBs (transformer oils)
- spent catalysts (e.g. hydrotreating catalysts)
- spent activated carbons
- · unsorted mixed plastics.

The basic chemical reactions that take place in a liquid phase hydrogen reactor are shown in Fig. 7a. As can be seen, the bond strength between a carbon and a heteroatom is increasing from chlorine over sulphur and

TABLE 6

VCC Syncrude qualities (Demonstration Plant Bottrop)

Product	Density (kg/L)	Qualities	Bottrop plant	Further use in Scholven refinery
Naphtha IBP-180°C	0.73	Sulphur, ppm Nitrogen, ppm	< 200 < 40	Refiner feed
Middle distillate 180-390°C	0.850	Sulphur, ppm Cetane number Cloud point, °C	< 1500 n.a. n.a.	Pool for diesel/ light heating oil
VGO 390–510°C	0.89	Sulphur, ppm CCR, wt.% Metals, ppm	< 10000 < 0.3 < 1	Feedstock to hydrocracker

nitrogen to the strongest carbon-carbon bond. Since the main intent of the process application is to convert residual oils into light products, mainly carbon-carbon bonds have to be cracked to achieve this goal. As the process has to operate under severe conditions, it is obvious that the much weaker bonds of carbon-heteroatom have already been cracked before the carbon-carbon bond gets refractive. Therefore, one can take advantage of this fact to convert in a commingled mode of operation crude derived vacuum resids together with waste materials. If, at the same time the amount of waste materials to be processed is limited to an amount which does not significantly effect the fluid dynamics of the reactor, the proven technology can be applied in a safe manner to recycle waste materials. The chemical reactions taking place and the products produced by processing trichlorobenzene and polychlorinated biphenyls is given in Fig. 8. Basically the chlorine is converted into HCl and is neutralized by calcium oxide to form calcium chloride. The organic part is transfered into cyclohexane, respectively biphenyl. Technically this is performed by mixing the waste material, the neutralization agent (Additive II), vacuum resid and the additive and routing it commingled to the LPH reactor. The formed chlorine salt shows up in the hydrogenation residue, whereas the organic components are forming part of the syncrude (Fig. 9).

Specifically with respect to transformer oils (PCBs), small scale tests had to be executed to demonstrate the feasibility of this basic considerations. After successful small-scale tests, the Bottrop Plant acquired a temporary permit to process PCBs under the stringent control of the permitting governmental agency in 1990. Since 1991 the plant holds permanent authorization for processing these materials as a result of its very successful operation, demonstrating that PCBs are completely destructed and the syncrude produced is free of any chlorine. Today the plant is operated on a mixture of refinery vacuum resid, PCBs, used lubricants, degreasing oils, spent solvents, spent refinery catalyst, etc. An example for processing of degreasing oil commingled with refinery vacuum resid is given in Table 7. As can be seen the produced syncrude is significantly upgraded in quality (C/H ratio, sulphur, nitrogen content) and

(a)
$$R - C \in \xrightarrow{H_2} R - H + H - C \in Hydrocracking$$

$$R - N \in \xrightarrow{H_2} R - H + H - N \in Denitrification$$

$$R - S - \xrightarrow{H_2} R - H + H - S - Desulfurization$$

$$R - C : \xrightarrow{H_2} R - H + H - C \in Hydrocracking$$

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(b)

Nitrogen and oxygen components are destructed totally. The formed hydrocarbons reflect the structure of the original PUR. The following PUR structure has been assumed:

The H₂ consumption is 9,4 wt.% corresponding to 1042 Nm³/t feed.

Yield structure.

Water	27,9 wt.%
NH ₃	13,3 wt.%
Methane	12,4 wt.%
Butane	22,5 wt.%
Hexane	33,3 wt.%
Sum	109 4 wt %

The foaming agents (CIHC resp. FHC) are dehalogenated into HCI resp. HF and are transformed into salts (neutralized) by adding CaO.

Fig. 7. (a) Main chemical reactions. (b) Reaction products of polyurethane under VCC hydrogenation conditions. (c) Product qualities derived from plastics hydrogenation via VCC compared to Arabian Light crude oil. (d) Recycling of mixed waste plastics via hydrogenation

free of chlorine. The typical feed and syncrude composition from a day-to-day operation for the Demonstration Plant is given in Fig. 10.

The economic advantage of processing the before mentioned waste materials is given by their zero to negative value. The following example explains the order-of-magnitude benefits for a 25000 BPD unit, processing one-third of waste materials.

(c)		VCC Products	Arabian Light Crude Oil
Naphta (C5-180 °C)			
Density 15 °C	g/ml	0,750	0,730
S	ppm	< 50	500 - 700
N	ppm	< 50	< 50
Middle Distillate (180-350 °C)			
Density 15 °C	g/ml	0,850	0,825
S	ppm	< 150	7400
Cetane Number		43 - 48	45 - 50
Vacuum Gasoil (< 350 °C)			
Density 15 °C	g/ml	0,900	0,920
S	ppm	< 500	25000
N	ppm	< 500	800
Metals	ppm	< 1	< 1
Residue (> 520 °C) (1)			
Density 15 °C	g/ml	ca. 1,30	1,012
S	wt.%	1,50	4,02
Metals	ppm	5000 - 7000 (2)	121
Ashes	wt.%	6 - 12	0,05

Remarks:

- (1) corresponds to hydrogenation residue of the VCC unit resp. the distillation residue from crude distillation
- (2) depends on type of plastics

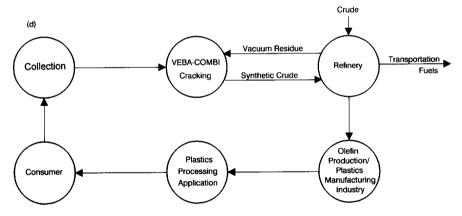


Fig. 7. (Continued)

Value of waste materials (free upgrader plant in Germany)

• Used lube oils \$\forall t approx. 0

• Materials ≤ 0.2 chlorine \$\frac{1}{200}\$ approx. 200–250

• Pure PCBs \$/t approx. 1500–1800

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

2HCI + CaO -- CaCl2 + H2O

Fig. 8. Mechanism of dechlorination reactions.

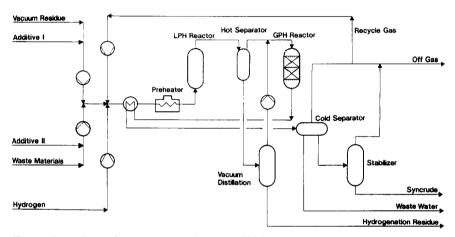


Fig. 9. Recycling of waste materials in the VCC process.

Savings (MM\$/year)

• 8330 BPD vacuum resid¹ 27

• Credits² from waste processing 110 $\sim 130-140$

This example illustrates drastically the high profitability of processing those materials, at least under the conditions prevailing in Germany.

The most recent development in feedstock processing was stipulated by the new plastic packing material ordonance in Germany, which calls for a high

¹ At 10\$/BBL (HFO).

² Density 1.2 g/ml.

TABLE 7
Chlorine decontamination and product qualities via VCC (Demonstration Plant Bottrop)

Parameter	Vacuum bottom (70%)	Residue from degreasing plant (30%)	Product
C (%)	85.03	83.49	87.03
H (%)	10.34	10.62	12.86
S (%)	3.34	0.98	0.0373
N (%)	1.18	0.92	0.0162
O (%)	0.6	3.7	0.05
Cl (ppm)	N.D.	10,200	< 1
IBP-200°C (%)	_	44	32
200-350°C (%)		22.1	41
350-500°C (%)	0.6	19.6	26
> 500°C	99.4	14.3	1

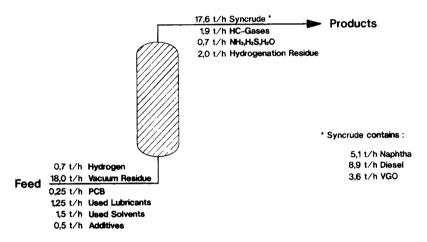


Fig. 10. Recycling of waste materials (VCC Demonstration Plant).

degree of recycling of mixed plastics to avoid unnecessary occupation of limited space on deposit sites. As thermal utilization is no longer permitted, the direct or chemical recycle results in

- protection of limited irrecoverable energy resources (crude oil)
- · avoidance of dioxine emission.

The VCC process, due to its capability to handle chlorines and solids is perfectly suited to process these materials. The results of plastics decomposition for polyurethane is given in Fig. 7b. Figure 7c gives a comparison of yields and qualities from processing mixed plastics compared to Arabian Light. As a result, unsorted mixed plastics are converted into residue free synthetic crude oils (SCO) which serve as feedstock for further olefins production (Fig. 7d). Thereby the loop from plastics production over utilization to olefins



Fig. 11. Areal view of the Demonstration Plant Bottrop.

is closed by the VCC process in an environmentally safe manner. After a demonstration of this way of chemical conversion, the Bottrop Demonstration Plant is presently debottlenecked to process 40000 t/year of unsorted mixed plastics from mid-1993 onwards.

Figures 11-13 give an impression of the Bottrop Demonstration Plant.

5. IMPACT OF A VCC-UNIT INTEGRATED INTO AN EXISTING REFINERY CONFIGURATION

For the purpose of illustrating the impact of the integration of a VCC unit into a refinery, reference is made to a 100000 BPSD standard refinery configuration processing Arabian Light crude.

The refinery configuration chosen consists of

- an atmospheric and vacuum unit
- refiner/reformer unit
- FCC including alkylate unit
- · gas treatment unit.

The setup is shown in Fig. 14.

For the purpose of total destruction of heavy fuel oil, a VCC unit is introduced into the refinery scheme (Fig. 15) converting the produced vacuum resid

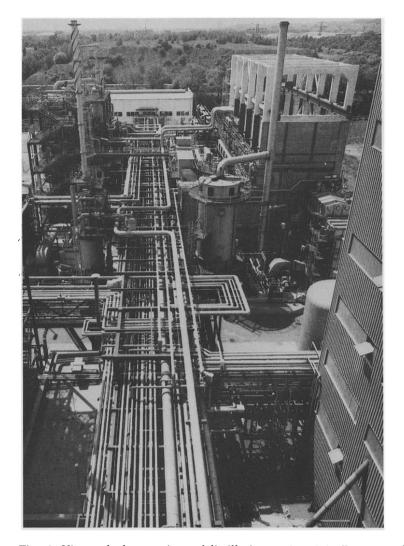


Fig. 12. View on hydrogenation and distillation section of the Demonstration Plant Bottrop.

plus the FCC slurry oil (HCGO). For the purpose of this evaluation it is assumed that the necessary hydrogen is generated by steam reforming of natural gas. In an optimized scheme the size of the steam reformer unit may be reduced by recovering hydrogen from the naphtha reformer off-gases. The impact on refinery product output by introducing the VCC residual oil conversion unit into the basic refinery scheme is given in Table 8.

The basic scheme—without bottoms upgrader—is producing approx. 89000 BPD transportation fuels. By introducing a VCC unit the remaining $\sim\!21000$ BPD HFO (vacuum resid+FCC slurry oil) are converted into light distillates with a volumetric yield of approx. 105%. A further yield improvement takes place by converting the high quality VCC VGO in the FCC unit



Fig. 13. Large volume reactor of the Demonstration Plant Bottrop.

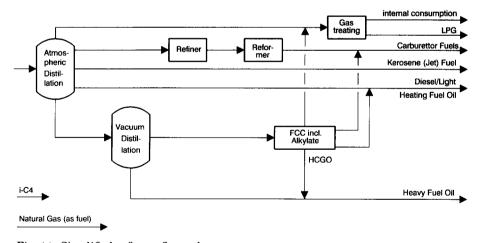


Fig. 14. Simplified refinery flow scheme.

(with connected alkylate unit). In total a yield improvement of 24500 BPD is achieved and no further HFO is produced. As VCC kerosene and diesel are of low aromatic content, the quality of the refinery pool for both products is significantly improved.

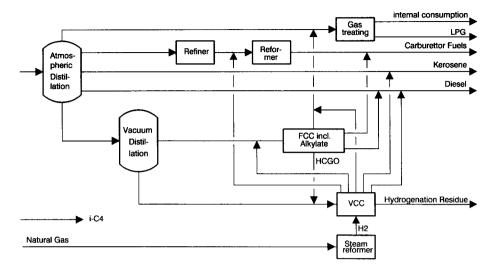


Fig. 15. Simplified refinery flow scheme with integrated VEBA-COMBI-CRACKING unit.

TABLE 8

Comparison of yields for a medium and high conversion refinery based on Arabian Light using VCC as high conversion process

	Medium conversion refinery	High conversion refinery
Crude oil import (BPD)	100 000	100 000
Products (BPD)		
Carburettor fuels	60 300	73 200
Kerosene	10 900	14 000
Diesel	17 700	26 200
Transportation fuels (BPD)	88 900	113 400
Heavy fuel oil (BPD)	21 200	-

6. CONCLUSIONS

During its recent years of operation the Bottrop Demonstration Plant has seen some important achievements

- · confirmation of all design data
- high reliability (≥91%)
- demonstration of the forgivingness (or robustness) of the technology
- demonstration of waste recycling for environmental protection, coupled with production of refinery feedstocks and economic improvement.

For a further extension of the waste recycling aspects the hydrogenation of mixed plastic material has been demonstrated at the Bottrop Demonstration

Plant. The plant is presently undergoing a debottlenecking program to process additionally 40000 t/year of this material as from mid-1993.

Especially the application of waste material conversion makes bottoms of-the-barrel upgrading attractive even in times of fluctuating differentials as this mode of operation results in robust economic behaviour in uncertain economic scenarios. Furthermore, the recycling of industrial waste streams contributes to a savings in irrecoverable resources and environmental protection as landfill or combustion is avoided.

BIBLIOGRAPHY

Lischer, H., Kretschmar, K., Niemann, K., Cotte, E., Guitan, J. and Marruffo, F., 1988. Deep conversion of heavy oil and bitumen via VEBA-COMBI-CRACKING—An update. Third Int. Conf. on Heavy Crude and Tar Sands, Long Beach, CA 22-31 July 1985. AOSTRA, Chap. 119, pp. 1263-1272.

Graeser, U., Kretschmar, K. and Niemann, K., 1983. Erdöl u. Kohle, 36(8): 362.

Graeser, U. and Niemann, K., 1982. Oil Gas J., 80(12): 121.

Graeser, U. and Niemann, K., 1983. Am. Chem. Soc., Div. Pet. Chem., Prepr., 28(3): 675.

Kretschmar, K., Lischer, H. and Niemann, K., 1986. Erdöl u. Kohle, 39(9): 418.

Niemann, K., Merz, L., Rupp, M. and Kretschmar, K., 1988. Gas phase hydrogenation in the integrated hydrotreating/hydrocracking unit of the VCC process. Paper presented at the ACS-Div. Ind. Eng. Chem. National Meeting, Toronto, June. Paper No. 2115S.

Döhler, W. and Rupp, M., 1987. Chem. Eng. Technol., 10:349.

Niemann, K., Kretschmar, K., Rupp, M. and Merz, L., 1989. Upgrading of Alberta derived bitumen applying the VCC-technology. Paper presented at the 4th UNITAR-Conf., Edmonton, Alta., August. AOSTRA, Vol. 5, Paper No. 65, pp. 225-246.

Wenzel, F. and Niemann, K., 1989. Paper presented at the 1989 NPRA Annual Meeting, San Francisco, CA, March.

Kretschmar, K., Merz, L., Niemann, K., Krasuk, J. H., Guitian, J. and Marruffo, F., 1988.
Process for the Hydrogenation of Heavy and Residual Oils. U.S. Patent Appl. No. 07/105290 (Notice of Allowance Dec. 19, 1988).