Oil & Gas Science and Technology – Rev. IFP, Vol. 54 (1999), No. 5, pp. 597-618

Gasification in Petroleum Refinery of 21st Century

E. Furimsky[1]

1 IMAF Group, 184, Marlborough Avenue, Ottawa, Ontario - Canada, K1N 8G4
e-mail: efurimsk@netcom.ca

Résumé — La gazéification dans la raffinerie du pétrole du XXIe siècle — Les tendances de la production mondiale de pétrole brut indiquent une augmentation continue de la part des bruts lourds. La progression du rendement en résidus de distillation s'accompagne d'une augmentation de la teneur en soufre. Des distillats supplémentaires peuvent être obtenus en traitant les résidus. Cette phase de valorisation génère des résidus finaux, comme les goudrons, le coke et l'asphalte, résultant respectivement de la viscoréduction, de la carbonisation et du désasphaltage. Les résidus finaux peuvent être, à leur tour, convertis en produits utilisables comme l'hydrogène, la vapeur, l'électricité, l'ammoniac et des produits chimiques. Dans ce contexte, la gazéification est apparue comme la technologie de choix pour la valorisation des résidus en raison de ses meilleures performances. De même, les boues de raffinerie peuvent être cogazéifiées avec les résidus finaux et devenir alors des produits valorisables.

Intégrée à la raffinerie de pétrole, la gazéification peut aider à résoudre les problèmes environnementaux liés à l'élimination des résidus et des boues. Les résultats économiques de la raffinerie peuvent également être améliorés. Les tendances de déréglementation du marché de l'énergie permettent aux raffineries de pétrole d'y pénétrer, soit toutes seules, soit en partenariat avec les fournisseurs d'utilités. Le potentiel de coproduction de produits chimiques et de vapeur avec l'électricité offre une souplesse de réaction permettant de répondre aux demandes du marché. L'intérêt de la technologie de la gazéification est commercialement démontré. Parmi d'autres, les gazéificateurs à lit entraîné sont les gazéificateurs de prédilection. Plusieurs projets commerciaux en Europe, en Asie et aux États-Unis font appel à un gazéificateur utilisant soit un système d'alimentation en suspension, soit un système d'alimentation par voie sèche.

Mots-clés : gazéification, résidus de pétrole, IGCC, électricité et produits chimiques, pollution.

***Abstract — Gasification in Petroleum Refinery of 21st Century** — The worldwide trends in the crude oil supply indicate a continuous increase of the heavy crudes. The increase in the yield of distillation residues is complemented by an increase in their sulfur content. Additional distillates are produced by upgrading the residues. The upgrading step generates final residues, such as visbreaking tar, coke and asphalt which are produced by visbreaking, coking and deasphalting, respectively. The final residues can be converted to usable products such as hydrogen, steam, electricity, ammonia and chemicals. For this purpose, gasification has emerged as the technology of choice because of its superior environmental performance when compared with the competing means for residue utilization. Also, refinery sludges can be cogasified with the final residues and as such, be converted to usable products.*

If integrated with the petroleum refinery, gasification can diminish any environmental problems associated with residue and sludge disposal. The economic indicators of the refinery can improve as well. The trends in deregulation of the power market enable petroleum refineries to enter this lucrative market either alone or in a partnership with the utilities. The potential of coproduction of chemicals and *steam with electricity offers the flexibility to respond to market demands. Gasification technology is commercially proven. Among several types, entrained bed gasifiers are the gasifiers of choice. A number of commercial projects in Europe, Asia and United States use a gasifier employing either a slurry feeding system or a dry feeding system.*

Keywords: Gasification, petroleum residues, IGCC, electricity and chemicals, petroleum refinery emissions.

INTRODUCTION

The evolution of supply and demand patterns and technical considerations indicate difficulties for disposing of refinery residues in the medium and long term [1, 2]. This is caused by a continuous decrease in the volume of conventional crudes which have to be replaced by heavier crudes. This is illustrated on the results in Figure 1 showing a continuous increase in the gravity and sulphur content of crudes which have been processed in United States refineries between 1983 and 1995 [3]. These trends have been continuing until now and it is anticipated that they will continue into the next century. The higher volume of heavy crudes results in the higher yield of residues. There are several options available to refiners for the residue disposal. This includes either using the residues without further processing or converting them into higher demand products using carbon rejection and/or hydrogen addition technologies. In some parts of the world, residues can be blended with a gas oil and sold as a heavy fuel oil. However, this outlet is drying out because of a continuous increase in the sulphur and metal contents of the residues. A further processing to obtain additional liquids is an attractive option being practiced by many refineries. The choice of the upgrading technology has to be thoroughly evaluated. Thus, according to Tamburrano [2], at least nine factors have to be taken into consideration. The stiffer legislative restrictions suggest that choice of the technology will be environmentally driven.

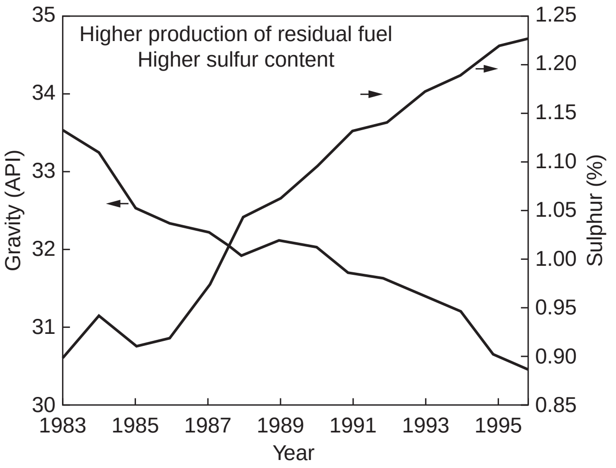

Figure 1

United States crude quality trends between 1983-1995.

In the case of the hydrogen addition technologies, problems with disposal of the spent catalysts have to be solved because of their classification as hazardous wastes [4].

Significant increase in coke production per unit of processed crude in United States between 1980 and 1990 indicated on coking technology gaining on importance, i.e., during this period, the coke production increased by 70% [3] . Since that time, the coke production has been steadily increasing. The sulphur content of coke has been increasing as well. This has resulted in a steady decrease in the price of the coke. Today, price per one ton of coke is less than $10 inspite of its highest heating value compared with the other solid fuels. Visbreaking is being widely practiced in other countries (e.g., Italy), whereas the suitability of deasphalting for the residue upgrading has been recognized as well [5, 6]. The trends in the yield and sulphur content observed for coke are similar for the residues produced from both visbreaking and deasphalting.

After a thorough evaluation of several factors, gasification was identified to be an answer to problems with the disposal of refinery residues [2]. This technology can convert any solid or semi-solid carbonaceous material to synthesis gas. This includes intermediate refinery streams, asphalt, petroleum coke and even various refinery sludges. The raw gas produced in the first step is cleaned to remove sulphur compounds and particulates. The former are converted into pure sulphur in the Claus plant, while particulates are recycled to the gasifier. Thus, almost 100% carbon conversion can be achieved. Metals (vanadium and nickel) are concentrated in the slag/ash, saleable for metal recovery. Thus, no solid byproduct is left for disposal. The clean synthesis gas can be converted to valuable products such as electricity, steam, hydrogen and chemicals. Gasification technology is commercially proven and used in many parts of the world. It is now being considered for the final conversion of refinery residues in Europe, United States and Asia. Electricity appears to be product of the main interest. For this purpose, the integrated gasification combined cycle (IGCC) technology is being applied. This technology can be readily integrated with a petroleum refinery. Thus, most of the components of an IGCC plant are part of a typical refinery. This is indicated by the simplified flowsheet of an IGCC plant (Fig. 2), which shows that the gasifier and feedstock preparation units may be the only units of the IGCC island not yet operated by the refinery. This ensures the availability of the qualified operators. Besides electricity generation, part of the synthesis gas can be converted to hydrogen for the refinery consumption or chemicals. Also, steam required for the refinery operation can be produced by the IGCC plant.

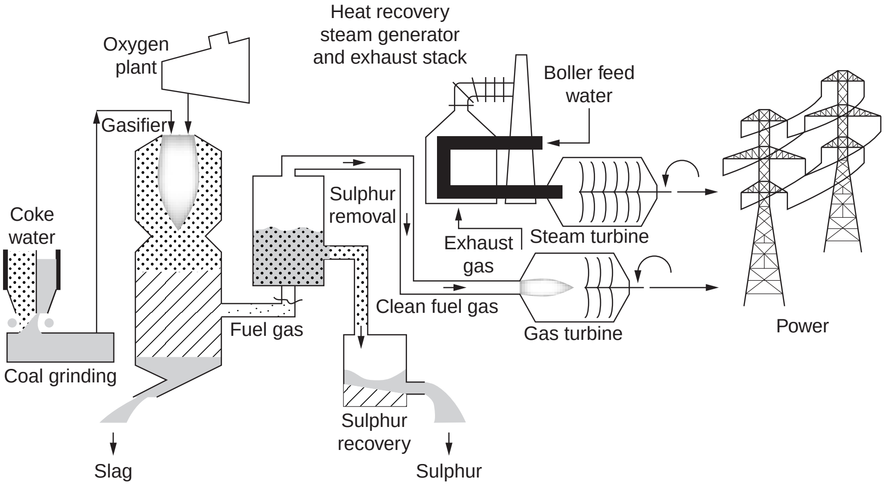

Figure 2

Simplified flowsheet of IGCC plant.

The integration of gasification with refineries offers new business opportunities to offset potential loss of a share of traditional refiner's market due to the introduction of reformulated gasoline containing oxygenates like MTBE, TAME, methanol, etc., as well as agricultural fuels like ethanol and biodiesel. Trends around the world indicate on the deregulation of the electricity market, one of the most lucrative and steady market. This enables petroleum refineries to enter this market either alone or in a partnership with utilities.

The environmental performance of IGCC technology is unmatched by competing means of dealing with low value refinery residues. Typical emissions from competing technologies for electricity generation were estimated by Bechtel [7] and are shown in Table 1. It is evident that the emissions from IGCC plants are the lowest and are in the range of those from combined cycle burning natural gas. The environmental acceptability was the major concern before the start of the construction of the IGCC plant at the El Dorado refinery in Kansas, United States [8]. In this case, the project had to obtain environmental permits including the prevention of significant deterioration permit. The environmental agencies such as United States *Environmental Protection Agency* (*EPA*) and *Kansas Department of Health and Environment* (*KDHE*) were involved together with *Texaco*. After necessary permits were received, the press release stated "*Texaco* and *KDHE* set a national precedent for using refinery waste products for fuel". The major commercial projects in different stages of development and construction are listed in Table 2. Strict environmental regulations were the driving force behind the choice of IGCC technology for commercial projects in Italy. In particular, the limits set by the *European Community Large Combustion Plant Directive* for new large plants have been extended to the existing plants. For this reason, in Italy, production of electricity from residue gasification is eligible for subsidies and incentives.

TABLE 1

Comparison of typical emissions from power generating technologies using petroleum coke (lb/MWh, 100% capacity, 5wt.% sulphur) [7].

Emissions	Natural gas comb. cycle	Gasification comb. cycle	Circulating fluid bed	PC boiler FGD and SCR
SO_2	0.0	0.6	3.7	3.6
NO_x	9.3	0.4	0.9	1.5
CO	0.2	0.4	1.5	NA
VOC	0.02	0.07	0.08	NA
Particulates	0.05	0.07	0.2	0.2
CO_2	820	1930	2170	2120
Solid waste	0	9.1*	350	190

* The solid from a coke gasifier contains only the feed metals and some carbon.

TABLE 2

Commercial projects for gasification of refinery residues

Location	Feedstock	Final product
Isab, Priolo, Italy	Residue from deasphalting	Power (500 MW)/steam/H_2
Saras, Cagliari, Italy	Visbreaking tar	Power (500 MW)/steam/H_2
API, Falconara, Italy	Visbreaking tar	Power (250 MW)/steam
Shell, Pernis, The Netherlands	Visbreaking tar	Power/steam
Thermie, Puertollano Spain	50/50 petcoke/lignite	Power (370 MW)
Kawasaki, Japan	Heavy residues	Power (545 MW)
Texaco, El Dorado Kansas, United States	Petcoke and sludges	Power/steam
Delaware City, United States	Petcoke	Power/steam

1 FUNDAMENTAL ASPECTS OF GASIFICATION

Gasification has been used commercially for many years. A wide range of gasification conditions can be attained by properly matching the feedstock with a type of gasifier. Thus, any solid, semisolid or liquid organic material can be gasified in accordance with environmental regulations. The simplified flowsheet in Figure 3 indicates potential final products produced from the synthesis gas obtained during gasification as the first step. Only a cursory account of this topic will be given in this review. Thus, an extensive information on various aspects of gasification can be found in the literature. In this regard, reports published by *IEA* [9-11] provide an excellent description of gasification technology.

Gasification is a partial oxidation process in which carbonaceous solids react with oxygen, enriched air or air according to the overall reaction:

$$C_nH_m + n/2\ O_2 \rightarrow nCO + m/2\ H_2$$

The overall reaction can be summarized in several basic chemical reactions such as gasification with O_2:

$$C + 1/2\ O_2 \rightarrow CO \qquad \wedge H = -\ 123.1\ \text{kJ/mol} \qquad (1)$$

combustion with O_2:

$$C + O_2 \rightarrow CO_2 \qquad \wedge H = -\ 405.9\ \text{kJ/mol} \qquad (2)$$

gasification with CO_2:

$$C + CO_2 \rightarrow 2\ CO \qquad \wedge H = 159.7\ \text{kJ/mol} \qquad (3)$$

gasification with steam:

$$C + H_2O \rightarrow CO + H_2 \qquad \wedge H = 118.9\ \text{kJ/mol} \qquad (4)$$

In overall, gasification is a controlled combustion in O_2 depleted atmosphere. In this case, most of the O_2 fed to the gasifier is consumed in Reactions (1) and (2). These reactions generate heat to increase temperatures at which chemical bonds are broken and gasification Reactions (3) and (4) become favorable. If the gas is considered for a subsequent synthesis, the water-gas shift Reaction (5), i.e.:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \wedge H = -\ 40.9\ \text{kJ/mol} \qquad (5)$$

also becomes important for adjusting H_2/CO ratio. Otherwise, the primary objective is to maximize content of combustibles such as CO and H_2. CH_4 can also be formed at low gasification temperatures. Sulphur in the feed is converted mainly to H_2S and small amount of COS. Traces of S_2 and CS_2 can also be formed. Most of the nitrogen in the feed is converted to N_2. However, small amounts of HCN and NH_3 are also formed. HCl is the main Cl-containing product formed during gasification.

Gasification medium has a major impact on calorific value (CV) of gasification products. When air is used, a low CV products are obtained because of a significant dilution effect, whereas a medium CV gas is obtained in the case of O_2 or O_2 enriched air. However, the use of air eliminates the air separation unit on the site though in some refineries such unit may be already in the operation. The O_2 concentration in the gasification medium has an impact on the gasifier design. Thus, high O_2 concentrations are used to attain high gasification temperatures required for certain feedstocks. Steam can be added with O_2 to maintain heat balance of the combustion and gasification reactions in the gasifier. A direct gasification in the steam only yields a medium CV gas. However, in this case, an external source of heat is required for the gasification reactions to occur. A direct CO_2 gasification may have a potential if a cheap source of CO_2 is available.

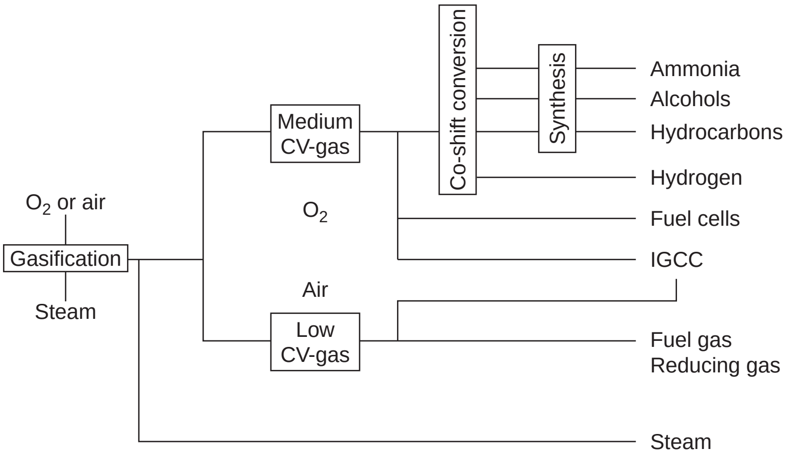

Figure 3

Slate of potential final products from gasification.

Also in this case, an external source of heat would be required. At high temperatures, CO_2 formed during combustion (Reaction (2)) will be converted to CO in the secondary gasification reaction (Reaction (3)).

Under certain conditions, gasification may be divided into two stages, i.e., primary gasification and secondary gasification. The former involves devolatilization of the feedstock. The secondary gasification involves gasification of the char from the devolatilization according to the reactions described above. In this regard, an efficient contact of the gasification medium with the hot char is crucial to attain high enough temperatures. Otherwise, the targeted composition of the gas produced as well as the form of solid residue cannot be obtained.

Temperature is directly related to the physical state of ash in the gasifier. There are three types of the operation, i.e., dry ash, ash agglomerating and slagging. During the dry ash operation (below 1000°C), the ash is removed dry without sintering. Depending on the composition of mineral matter, the ash agglomeration occurs between 1000 and 1200°C. As ash becomes sticky, the particles form agglomerates which are withdrawn at a controlled rate to maintain a steady state in the gasifier. Slagging of ash begins above 1200°C. It is essential that the fusion properties of the feedstock mineral matter are suitable for the slagging operation. Thus, it may be difficult to slag mineral matter which has a high fusion temperature unless a fluxing agent is added to decrease the temperature. High temperatures (~1500°C) used during slagging operations ensure high reaction rates, high gasification conversions, good quality gas and high feedstock throughputs. Slagging operation is also suitable for a great variety of the feedstocks.

2 ORIGIN OF REFINERY RESIDUES FOR GASIFICATION

The flowsheet of the refinery processing a conventional crude is shown in Figure 4a [12]. The crude oil entering the refinery is first desalinated before being processed by atmospheric distillation. The liquid fractions are further treated to meet the specification of transportation fuels and fuel oils. In this case, the atmospheric residue represents a small portion of the crude entering the refinery. In some situations, the atmospheric residue can be directly utilized as a heavy fuel oil. A vacuum gas oil can be obtained if the atmospheric residue is subjected to vacuum distillation. The vacuum residue usually meets the specifications of asphalt, a marketable construction material. Thus, in the case of some conventional crudes, an almost complete utilization may be achieved, leaving no residue. In such situations, there may be little economic incentive for an additional conversion of vacuum residues to liquid products. Besides increasing yields of liquid fractions by subjecting the atmospheric residue to vacuum distillation, the additional liquids can be obtained by further upgrading the residue from vacuum distillation. The typical upgrading options, such as coking and deasphalting are included in the flowsheet of the refinery shown in Figure 4b [12]. In this case, the upgrading processes generate the final residue such as coke and asphalt, which may be converted to usable products, i.e., it can be either combusted or gasified to generate electricity or other products.

The type of crude oil processed by the refinery and the conditions to which the crude oil is subjected determine the characteristics of the final residue. In the latter case, the selected process is essential. For heavy crudes, the upgrading of vacuum residues can significantly increase the yield of liquids per unit of crude entering the refinery. The best known upgrading technologies which generate the final residues can be divided into thermal processes and solvent extraction and/or precipitation processes. Catalytic hydroprocessing upgrading processes may not generate final residues. Thus, the residual pitch produced may be further upgraded to liquid products and final residues, e.g., coke or asphalt. Visbreaking (thermal or hydrogen) and coking (delayed, fluid and flexi) are typical thermal processes, whereas deasphalting is the best known solvent treating process [12, 13-15]. The typical yields of the final residues generated by these processes are shown in Table 3 [16]. In this case, the vacuum residue obtained from the Light Arabian crude was used as the feedstock for the corresponding process. Besides residues from vacuum distillation of the virgin crude, the feedstock for the upgrading process can originate from vacuum distillation of hydrocracked products [17]. The world residue upgrading capacity, including both carbon rejection processes and hydrogen addition processes is shown in Table 4 [18]. The former accounts for almost 80% of the total capacity, not including the residue FCC capacity.

TABLE 3

Yileds of final residues from vacuum residue derived from Light Arabian crude [16]

Process	Visbreaking	Deasphalting	Delayed coking	Flexicoking
Yield (wt.%)	81.8	26.0	32.8	15.5

TABLE 4

World residue processing capacity, Mbpd [18]

Technology	United States	Japan	Europe	Rest of world	Total
Carbon rejection					
Visbreaking	130	20	2170	1650	3970
Coking	1860	60	630	1220	3770
Deasphalting	260	20	10	100	390
Hydrogen addition					
Fixed-bed	500	580	150	810	2040
Ebullated-bed	110	25	25	180	340
Slurry phase	-	-	5	5	10
Residue FCC	630	250	210	740	1830
Total	3490	955	3200	4705	12 350

a

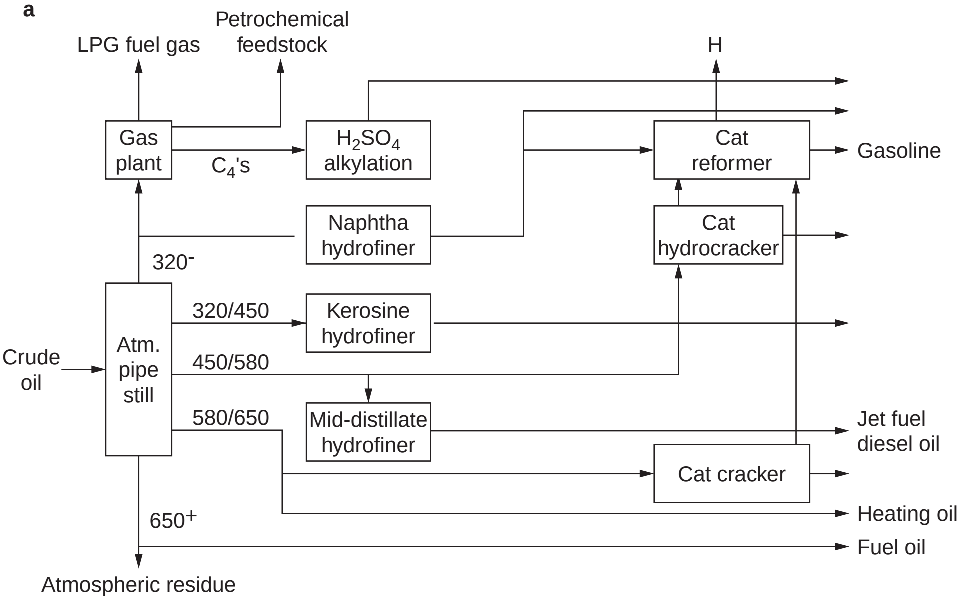

Figure 4a

Flowsheet of petroleum refinery; processing conventional crude.

b

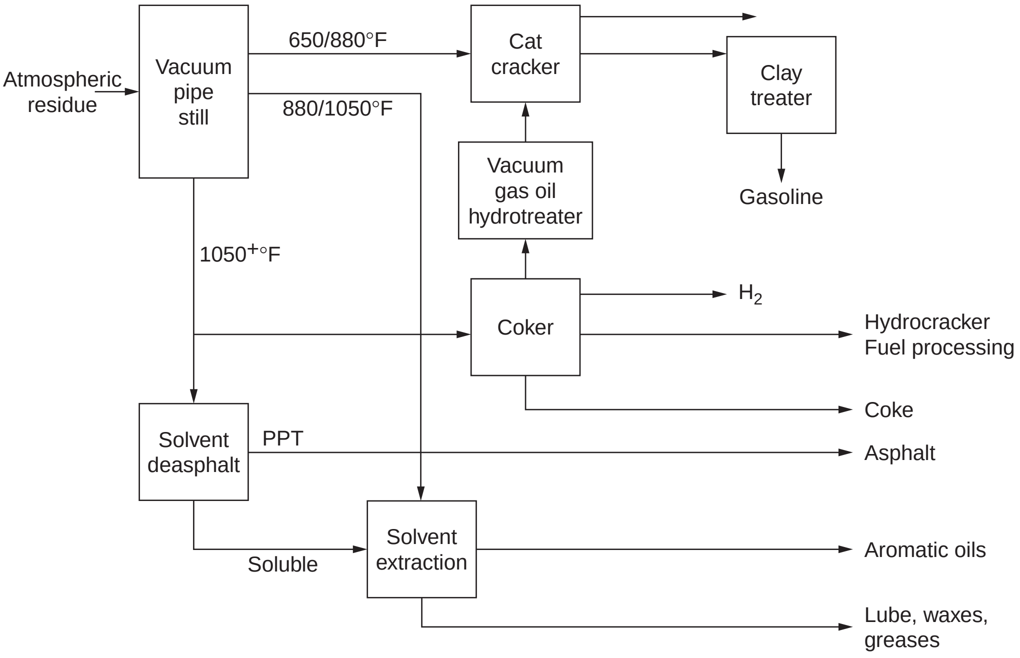

Figure 4b

Flowsheet of petroleum refinery; with residue upgrading option.

3 PROPERTIES OF THE FINAL RESIDUES

The primary focus will be on the properties which influence the gasification performance and feedstock preparation. The compositional data obtained from the proximate and ultimate analysis, ash composition, ash fusion and heating value of the feedstock provide essential information for predicting gasification performance. Also, this information is crucial for the material selection for critical parts of the IGCC plant. The physical properties, such as particle size distribution, grindability and slurrability are important for feedstock preparation. A vast database on the same properties of coals is available in the literature. A similar database for the final refinery residues is less extensive. However, by ash playing an insignificant role compared with the coals, predictions of the behavior of the final residues during gasification are more accurate. If the final residue is in the solid phase, such as cokes, the feedstock preparation and feeding are quite straightforward. In the case of visbreaking tars and pitches, specially designed systems are available to enable feeding in the molten phase. In some cases, a gas oil may be added as a diluent to improve feeding to the gasifier.

3.1 Cokes

It is believed that the most detailed information on properties of petroleum cokes was published by Bryers [19]. The compositional data and ash analysis, published in this article are reproduced in Tables 5 and 6, respectively. Important information on properties of the delayed coke was published by Bechtel [7]. Although properties of the feed influence properties of the coke, the effect of processing conditions is quite evident from the results in Table 5. In this regard, the content of volatiles, carbon and hydrogen are the best indicators of the severity to which the coke was subjected. As one would predict, based on the process conditions, the content of volatiles and hydrogen was largest for delayed coke and lowest for flexicoke. The significant difference in H/C ratio among the cokes indicates the degree of aromatization. Also, this reflects the difference in the severity of the processes. This may have a direct effect on the gasification reactivity, if the same particle size of the delayed and flexicokes is used for comparison. Thus, the reactivity of the latter is significantly lower. Properties of the feed from which the cokes were prepared influenced parameters such as the content of ash, nitrogen and sulphur.

The chemical composition of the cokes ashes is entirely determined by the properties of the mineral matter contained in the feed from which the cokes were derived. In this regard, the high content of NiO and V_2O_5 in the ashes from the delayed coking and flexicoking would indicate more conventional type feeds compared with the fluid coke, in which case SiO_2, Al_2O_3 and Fe_2O_3 account for most of the ash. Thus, the small amount of clay like species are usually present in heavier crudes. The ash composition determines the fusion properties.

TABLE 5

Properties of petroleum cokes [19]

Property	Delayed coke		Fluid coke		Flexi coke	
	1	2	1	2	1	2
Proximate, wt.%						
Fixed carbon	84.47	83.20	90.48	91.50	95.27	94.90
Volatiles	8.52	6.48	3.93	4.94	1.77	1.25
Ash	1.06	1.72	0.31	1.32	2.50	0.99
Moisture	5.96	8.60	5.28	2.24	0.46	2.86
Ultimate, wt.%						
Carbon	83.44	81.12	82.28	84.41	92.31	94.90
Hydrogen	3.35	3.60	1.74	2.12	0.68	0.30
H/C	0.48	0.53	0.25	0.30	0.09	0.04
Nitrogen	1.71	2.55	1.83	2.35	1.52	1.11
Sulfur	4.45	4.37	5.32	6.74	2.49	2.74
Oxygen	0.04	0.04	1.41	0.82	0.04	0.00
High heating value (Btu/lb)	14 530	14 298	13 325	14 017	14 057	13 972
Hardgrove index	54	-	35	-	55	-

TABLE 6

Typical ash analysis of various types of cokes [19]

Component	Delayed coke	Fluid coke	Flexi coke
SiO_2	10.1	23.6	1.6
Al_2O_3	6.9	9.4	0.5
TiO_2	0.2	0.4	0.1
Fe_2O_3	5.3	31.6	2.5
CaO	2.2	8.9	2.4
MgO	0.3	0.4	0.2
Na_2O	1.8	0.1	0.3
K_2O	0.3	1.2	0.3
NiO	12.0	2.9	11.3
V_2O_5	58.2	19.7	74.5
Ash fusion, °C red. atm			
ID	1540+	1378	1540+
ST (sph.)	1540+	1386	1540+
ST (hem.)	1540+	1439	1540+
FT	1540+	1474	1540+
Ash fusion, °C oxid. atm			
ID	1374	1095	749
ST (sph.)	1425	1155	791
ST (hem.)	1432	1183	853
FT	1433	1224	1312

The fusion temperatures in the reducing atmosphere are of primary importance because they are an indication of the slagging tendency of the ash during entrained bed gasification. It is evident from these results that the ashes from the delayed coking and flexicoking will not slag without the addition of a fluxing agent in the *Texaco* gasifier. However, the information published by *Shell* [3] suggests that more than 90% of the ash, having a composition similar to that of the flexicoking ash, slagged in the *Shell* gasifier. This slag was classified as non-leachable. In view of the high vanadium and nickel content, these ashes and slags can be considered as a high value by-product saleable to metal reclaimers. The disposal of the gasification slags is of little concern because they are non-leachable. As can be predicted, the high content of vanadium is responsible for the significant decrease in fusion temperatures in the oxidizing atmosphere. Therefore, the fusion temperatures of the delayed coke’s ash in the oxidizing atmosphere shown in Table 6 [19] should be reexamined.

With respect to feeding, the particle size of the coke is crucial. In entrained bed gasifiers, the mean particle diameter is about 40 microns. Therefore, significant crushing will be required for the delayed coke which is produced in the form of large lumps, compared with the fluid and flexi cokes which are produced in a powder form. Nevertheless, the Hardgrove index in Table 5 shows a lower hardness for the delayed coke than for the fluid coke. The particle size is perhaps the main parameter in narrowing down the gasifier selection to the entrained bed in the case of the fluid and flexi cokes.

3.2 Other Final Residues

In this case, the asphalt from deasphalting, visbreaking tar and in some circumstances even vacuum residues may be included among the final residues for gasification. The choice depends on the overall operating strategy of a refinery. The elemental analysis of several gasification feedstocks tested as liquid feedstocks is shown in Table 7 [20]. The H/C ratio of these materials is significantly higher than that of cokes suggesting that some liquids can still be produced, e.g., by coking. Nevertheless, for various reasons, the refiner may decide to include these materials among the final residues.

From the feeding point of view, physical properties such as the softening point, viscosity and pumpability are equally important as is the particle size for the solid feedstocks. In this regard, the asphalt from deasphalting deserves attention because its properties can be, to a great extent, influenced by the operating conditions applied during deasphalting. The results in Table 8 show the effects of different solvent on the asphalt properties from the Rose deasphalting process using the vacuum residue derived from the Light Arabian crude [21]. In this case, the asphalt can be handled as a solid and fed into the gasifier in a pulverized form or in a water slurry form. Thus, at ambient temperatures, the asphalt is very brittle and can be readily crushed, as indicated by the Hardgrowe index exceeding 80. As rather high viscosities suggest, feeding of such materials in a molten phase could be difficult. However, there are some asphalts from deasphalting having a softening point lower than 100°C [12, 22]. Besides the type of solvent and solvent/oil ratio, the origin of the deasphalted feedstock determines the properties of the asphalt. The type of deasphalting process can have an impact on the properties of the asphalt as well.

TABLE 7

Properties of liquid and semiliquid residues [20]

Property	Heavy fuel oil	Vacuum residue	Asphalt from deasphalting	H-Oil bottoms	Eureka pitch
Spec. gr. Kg/m^3	0.98	1.04	1.19	1.08	1.16
Elemental (wt.% carbon	84.6	83.8	85.9	87.7	85.8
Hydrogen	10.0	9.6	9.5	9.3	6.0
H/C 1.42	1.38	1.33	1.27	0.84	
Nitrogen	0.4	0.6	1.4	0.7	1.2
Sulphur	4.5	6.2	2.4	2.3	5.2
Oxygen	0.4	-	0.5	-	1.6
Ash 0.1	0.1	0.3	-	0.2	

TABLE 8

Effect of solvent on properties of asphalt [ref. 22]

Property	Solvent	
	n-Pentane	*n*-Butane
Yield (wt.%)	19	32
Spec. gr. (Kg/m^3)	1.165	1.141
API	-10.0	-7.4
Sulphur (wt.%)	8.6	7.4
Nitrogen (wt.%)	0.9	0.7
Total metals (ppm)	455	325
Conr. carbon	60	47
Viscosity (cSt) At 450 F At 550 F	 101 000 3 700	 1 600 190
Ring and ball soft. point °F/°C	400/204 – 285/141	

A wide range of properties of vacuum residues and visbreaking tars (vacuum residue of visbreaking product) can be found in the literature. The softening point of these materials varies between 50 and 100°C but rarely exceeds 100°C. They can be fed into the gasifier in a liquid form, although in some case, the addition of a viscosity depressant may be required. An example of the effect of visbreaking on the properties of the visbreaking tar compared with that of the vacuum residue from which the tar was derived is shown in Table 9 [15]. It is to be noted that the vacuum residue is much heavier than the tar. Parameters such as gravity and viscosity are of particular interest. Thus, while the gravity of the tar has increased (API gravity decreased), the overall viscosity was reduced significantly suggesting improved pumpability of the tar compared with the vacuum residue. In this case, the tar accounts for more than 80% of the original vacuum residue.

TABLE 9

Properties of vacuum residues and corresponding visbreaking tar [15]

Property	Vacuum residue (+ 565°C)	Visbreaking tar (+ 350°C)
Yield (wt.%)	NA	81.9
API gravity	6.6	4.0
Viscosity, SSF 100°C	900	440
Sulphur	4.29	4.55
Conr. carbon	21.1	NA

3.3 Refinery Sludges

A variety of sources from petroleum refineries generate large volumes of different waste oil sludges, such as tank bottom/cleaning sludge, dissolved and induced air flotation skimmings and impoundment sludge. According to the EPA regulations, these sludges are included among so called K-wastes (Table 10). The sludges contain oil, emulsion, water and solids. The ratio of these phases vary from one application to another and from site to site. The difficult part of the sludge is the oil-water-solid emulsion phase, which is always present. This phase represents a distinct phase for separation in combination with water and solid phases. The emulsion phase is stable and cannot be broken by centrifugal and filtration methods but can be partly destabilized by heating. The customary method of refinery sludge management involves storage in ponds and tanks, from where it has to be taken for final disposal. Some disposal and utilization options for refinery sludges were discussed by Kanakamedala and Islam [23]. In addition, the current EPA regulations allow utilization of the waste sludges in the coker units. It is believed that the injection of the sludges into an entrained bed gasifier would provide an even more efficient method for sludge utilization. This point was raised by Falsetti *et al.* [24] while discussing gasification of petroleum coke in the *Texaco* gasifier. In this case, the sludge could enter the system during the preparation of the coke-water slurry to be fed to the gasifier.

TABLE 10

Refinery K-wastes

K048	Dissolved air flotation (DAF)
K049	Slop oil emulsion
K050	Heat exchanger bundle sludge
K051	API separator sludge
K052	Tank bottoms

4 GASIFICATION PROCESSES

Gasification processes may be operated either at a near atmospheric pressure or at an elevated pressure. The effect of pressure up to about 3.0 MPa (440 psi) on product composition is small although the equilibrium considerations suggest on slowing down the decomposition of steam and CO_2 with increasing pressure. Many of the downstream units operate at elevated pressures. Then, if the gasifier operates at a near atmospheric pressure, the raw gas has to be compressed for the further processing. The cost of this compression may exceed the cost of an atmospheric gasifier compared with the pressurized gasifier. Therefore, most of the advanced commercial or near commercial gasifiers operate at elevated pressures. The simplicity of gasification chemistry is overridden by the mechanical complexity as well as the material requirements. A steady and uninterrupted feeding of the feedstock must be maintained to ensure a continuous operation. Further, a proper mixing of the feedstock with gasification medium in the gasifier must be achieved to obtain high conversions. Expensive refractory linings are needed to prevent corrosions by slags in the advanced gasifiers. Superalloys have to be used for some heat recovery systems to prevent corrosions by sulphur, chlorine and alkalis and erosion by particulates. Several types of commercial gasifiers are available to deal with these problems.

The technical literature on gasification processes is rather extensive [9-11]. In this review, a brief summary will only be given with the emphasis on commercial gasifiers.

Fixed bed gasifier, also referred to as a moving bed gasifier, requires a feedstock particle size of 2 to 50 mm and can be used with air, oxygen and steam which are introduced into the bottom of the reactor. Feedstock is fed from the top, ash or slag leaves the bottom and produced gas exits at the top. Depending on the gasification medium, the bottom of the reactor can be operated either in a dry mode or in a slagging mode. In the former case, temperature in the gasification zone is in the range of 800 to 1050°C whereas in the slagging mode, the temperature may approach 1400°C. Reactors can be operated at pressures ranging from 0.1 to 3.0 MPa. Residence time is in the order of 1 to 3 h. This type of gasifiers may not be suitable for gasification of refinery residues, such as the fluid coke and flexi coke as well as visbreaking tar and asphalt from deasphalting.

In the fluidized bed gasifier, feedstock is injected into the bottom and reactant gases can be injected at two levels to maximize carbon conversion. The temperature in the fluidized bed gasifier may approach 1200°C if oxygen is used as gasification medium. The main problem of the fluidized bed systems is the extent of carbon conversion and the carry-over of the fine particles. Normally, this carry-over has a high carbon content and has to be collected and recycled to the gasifier. Also, the required average particle size (approximately 8 mm) of the feedstock exceeds that of the fluid coke and flexi coke. For delayed coke, the suitable particle size may be attained. However, low reactivity of the delayed coke may require a long residence time which translates into lower throughputs. Little information indicates on the use of the fluid bed gasifier for the gasification of the visbreaking tars and asphalt from deasphalting. High overall conversions can be achieved if the fluid bed gasification is combined with the combustion of the carried-over fines. In this case, both fluid coke and flexi coke can be used as feedstock. To a certain extent, limestone can be injected into the fluidized bed of the feedstock for the *in situ* sulphur capture. However, for feedstocks containing more than 5wt.% sulphur, the use of limestone in the fluid bed combustor is not recommended [25, 26]. Several types of the fluid bed gasifiers, e.g., U-Gas, HTW and KRW are available commercially. The gasification of petroleum coke containing about 2wt.% sulphur with the limestone injection was successfully demonstrated in KRW gasifier.

Entrained bed gasifiers require a pulverized feedstock of which about 90% is less than 200 mesh. This suggests that the fluid coke and flexi coke require only a little preparation. The feedstock can be injected either dry or in the form of a water slurry. Semisolid feedstocks, such as visbreaking tars as well as the asphalt from deasphalting can be injected in a molten phase. The injection ports can be either at the side or at the top of the reactor. In a dry feeding mode, the feedstock is screw-fed from lock hoppers to burners where the gasification medium (air, oxygen or steam) convey the feedstock at a velocity in excess of flame propagation rates into the reactor. Pumps are used for the injection in a slurry mode and the feedsstocks in a molten phase. Once in the reactor, particles are rapidly devolatilized and lose any inherent characteristics of the original feedstock. The high operating temperature effectively destroys all hydrocarbons, tars, oils and phenols which may be formed during the devolatilization. This reduces gas purification and eliminates water condensate contamination problems. The rapid reaction rate requires control to prevent an excess of oxygen, should the feeding be interrupted. There is no reservoir of carbon as is available either in the fluidized bed or fixed bed. The temperature of gasification flame may exceed 1500°C. As the result of the high temperature, most of the mineral matter in the feedstock is melted and removed in the form of a slag. Residence time is in the order of 1 s. The units are usually operated at high pressures. As indicated above, the combination of factors such as high temperatures, high content of contaminants in the vapor phase and molten mineral matter results in special material requirements.

Several types of the commercial entrained bed gasifiers are available for selection of one which fulfils best the performance, economic and environmental requirements. With respect to the gasification of refinery residues, the entrained bed gasifiers are the gasifiers of the choice. For the purpose of this study, these gasifiers will be discussed in more details. The best known slurry feeding entrained bed gasifiers are *Texaco* and *Destec*, whereas the best known dry feeding systems are *Shell* and *Prenflo* gasifiers. High temperatures attained in these gasifiers make them suitable for the gasification of less reactive feedstocks such as the petroleum coke and oil sand coke. In the case of the slurry fed gasifiers, refinery wastes such as K-, D- and F-wastes can be cogasified with the coke. A wide range of liquid and semisolid materials can also be gasified.

Prior to their utilization, gasification products have to be cleaned to remove particulates and sulphur. For this purpose, conventional cleaning systems are being used commercially. In this case, the gas is cooled and then scrubbed to remove particulates. A low temperature steam can be recovered during the low temperature cooling of the particulate free gas. Also, this gas can be used to preheat water for fuel gas saturation prior to combustion in the turbine or to preheat boiler feed water. In refinery, this gas can be used to preheat other streams. The particulate free gas enters the COS hydrolyzer where most of the COS is converted to H_2S in the presence of a catalyst. This fuel gas then enters the acid gas removal section where more than 95% of sulphur is removed. For this purpose, various commercial processes operated at about 100°C, e.g., Selexol, Sulfinol, Stretford, etc. are available. Attempts are being made to develop a hot gas clean-up process operating above 400°C. The selection of the process depends on the system parameters and concentration of acid gases. After desorption from the scrubbing agent, the acid gases enter Claus process for recovery of elemental sulphur. An additional treatment of the tail gas from the Claus process is needed to meet environmental regulations. This is carried out in the Scot process. It is noted that most of the components of the gas cleaning systems are in the operation in refineries for purifying refinery gas prior to their use either as petrochemical feedstocks or combustion fuel.

4.1 *Texaco* and *Destec* Gasifiers

Texaco and *Destec* are the most advanced slurry fed gasifiers. In the *Texaco* process, the solid feedstock such as coke is pulverized and slurried in a wet grinding mill to produce a pumpable slurry containing between 55 and almost 70% of solids. The slurry water consists of the recycled condensate from raw gas cooling and a make-up water. The slurry is fed to the gasifier through a specially designed nozzle together with oxygen. The slurry fed system provides high feeding reliability which is critically important for pressurized systems. However, the use of the slurry feeding system introduces a thermal penalty since some of the heat of combustion must be utilized to convert the slurry water to steam. As the water requirements for the slurry production increase, the oxygen consumption increases and quality of the gas decreases. It is therefore critical for the economy of the *Texaco* process that the solid concentration in the slurry is high. In this regard, in the solid concentration range, low rank coals and lignites are at the low end and cokes at the high end. It is expected that for cokes, the solid concentration in the slurry can approach 70% [25]. Semisolid feedstocks such as vacuum residues and visbreaking tars as well as liquid hydrocarbon feedstocks can be injected in a molten or liquid form without requiring the slurry preparation. The synthesis gas production from the delayed and fluid petroleum cokes is compared with two United States coals in Table 11 [27]. The solid carbon concentration in the slurry is 53, 48 and 41 for the petroleum cokes, Pittsburgh 8 and Utah coals, respectively. In this case, the size of the plant approaches that of the Cool Water gasification plant in California, i.e., about 100 MW electricity.

TABLE 11

Synthesis gas production from coals and cokes [27]

	Coal		Coke	
	Pittsburgh 8	Utah	Delayed	Fluid
Feed rate				
Feedstock, MT/D	907	907	907	907
Oxygen, MT/D	836	795	1080	1030
Water, kg/h	20 360	25 170	24 263	24 671
Dry analysis (wt.%)				
Carbon	74.16	68.21	88.50	85.98
Hydrogen	5.15	4.78	3.90	2.00
H/C	0.83	0.84	0.53	0.29
Nitrogen	1.18	1.22	1.50	0.98
Sulphur	3.27	0.37	5.50	8.31
Oxygen	6.70	15.69	0.10	2.27
Ash	9.54	9.73	0.50	0.46
High heating value				
Btu/lb	13 600	11 800	15 400	13 800
kcal/kg	7540	6570	8550	7665
Product composition (mol%)				
CO	39.95	30.88	46.20	47.14
H_2	30.78	26.71	28.69	24.33
CO_2	11.43	15.91	10.68	13.16
H_2O	16.43	25.67	12.37	12.67
CH_4	0.04	0.22	0.17	0.09
N_2 + Ar	0.49	0.50	0.55	0.42
H_2S + COS	0.88	0.11	1.34	2.19

Texaco gasifier is a cylindrical refractory lined vessel mounted on the top of the radiant cooler. It has no movable parts, so its maintenance is simple. It operates at temperatures ranging from 1200 to almost 1400°C and pressure of about 30 atm. Depending on the final product, three versions of the Texaco process are available for commercial uses. The differences among these versions are based on the extent of heat recovery from hot gasifier products. In the case of the radiant + convective design (Fig. 5), hot gasifier products exit gasifier at the bottom and enter radiant cooler that generates high pressure steam. At the bottom of the radiant cooler, slag drops into a quench pool of cooling water prior to its removal, while gas flows to a convection type exchanger, where additional high pressure steam is generated. Cooled gas is further treated to remove particulates and sulphur to make it suitable for combustion turbine. High pressure steam generated in the radiant and convective coolers is injected into the steam turbine. This version of the *Texaco* process, termed as a full heat recovery design, is used for IGCC applications in which electricity is the main final product. Radiant only design incorporates radiant cooler only. Thus, no convective cooler is provided. Also, both the slag and the gas are quenched at the bottom. Cooled gas flows directly to the downstream units. These heat recovery design configurations significantly influence the degree of integration required by the IGCC plant. The main difference is in the quantity of high pressure steam which has an impact on the overall thermal efficiency of the plant. In the case of the total quench design, both the radiant and convective coolers are eliminated. This design offers a flexibility for coproduction of hydrogen, chemicals and electricity. Such design of the *Texaco* gasifier was used in the El Dorado refinery for gasification of petroleum coke and refinery sludges [8]. There is a significant difference in the cost of these designs being the highest for the full recovery and the lowest for the direct quench design.

Destec gasifier comprises two stages, i.e., a slagging first stage and a non-slagging second stage. In both sections, the preheated oxygen and slurry are fed and atomized through two opposing burner nozzles. The slagging section is a horizontal refractory lined vessel in which the feedstock slurry is partially combusted with oxygen. High temperatures (approaching 1400°C) ensure almost complete gasification of the feedstock while mineral matter is fused to a molten slag and drops to the bottom from where it is continuously removed. The hot gasification products from the slagging section enter the second non-slagging section which is a vertical refractory-lined vessel. Additional slurry is injected to the second stage to cool the gas. Also, in this section, the feedstock undergoes devolatilization and pyrolysis thereby generating additional gas of a higher heating value because no oxygen is introduced into the second stage. The endothermic gasification reactions occur as well. Particles of the unreacted feedstock are carried out with the gas. The temperature of the gas exiting the second stage may approach 1000°C. This gas enters the heat recovery

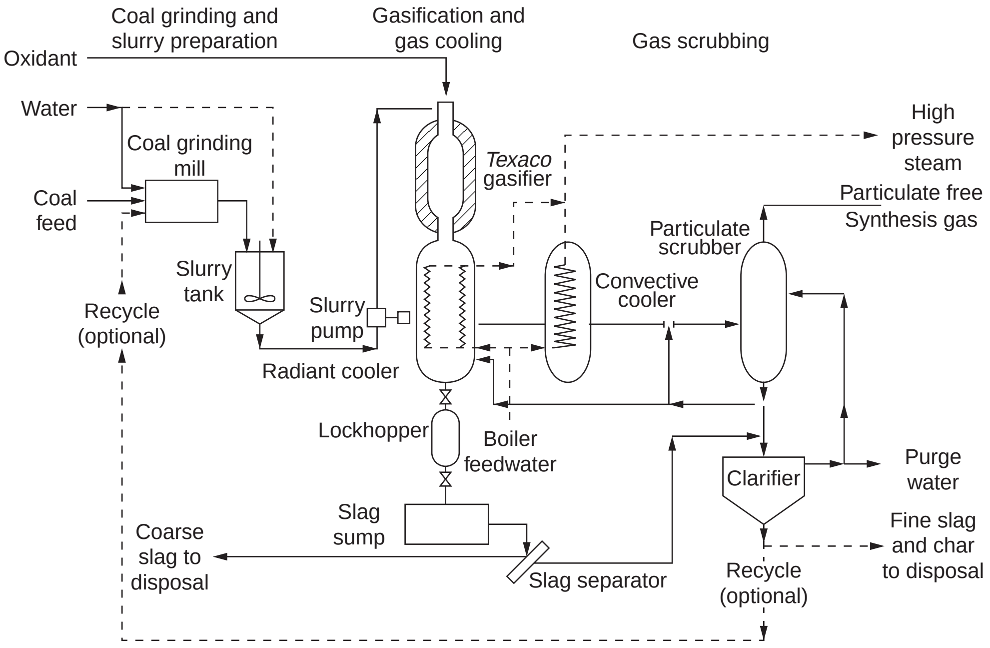

Figure 5

Flowsheet of gasification system employing *Texaco* gasifier with full heat recovery option.

boiler where a high pressure steam is produced. After the heat recovery, the particles are removed by a filter and recycled to the gasifier. The units downstream of the syngas cooler are similar as those shown in Figure 5.

There is no information in the technical literature indicating the use of the Destec gasifier for gasification of the petroleum coke and/or other refinery residues. A low volatility and reactivity of the petroleum coke suggest that the contribution of the second stage to the overall gasification will be small though a high carbon conversion in the first stage can be achieved. Nevertheless, high volatile low rank coals were the predominant feedstocks used during the all stages of the development of this gasifier. It is believed that some reactor modifications would be needed to make the *Destec* reactor more suitable for the gasification of petroleum coke. However, because of the slurry feeding system employed, the *Destec* gasifier may be used for cogasification of coal with refinery sludges.

4.2 *Shell* and *Prenflo* Gasifiers

These are the most advanced dry fed entrained bed gasifiers. In this case, coal is first pulverized and dried, if necessary, to less than 5% moisture content before is being conveyed pneumatically under nitrogen and pressurized in the lockhoppers. Then, the coal is fed to the gasifier together with oxygen and steam (if used) through two pairs of the horizontally opposed burners. Temperature in the gasifier can readily exceed 1500°C. At such temperatures, even a high fusion temperature mineral matter can be slagged. The vertical *Shell* gasifier shown in Figure 6 employs a water cooled membrane wall covered with a protective layer of a refractory and frozen slag. This arrangement allows recovery of the part of the heat generated in the gasifier in the form of superheated high pressure steam. Most of the molten slag is drained from the gasifier through a slag tap at the bottom and collected in the water bath. Part of the slag is entrained with the gas as a fly slag. The hot raw gas is first quenched with recycle product gas to about 930°C to solidify entrained fly slag. The gas and fly slag then flow to a convective gas cooler where most of the sensible heat of the gas is recovered as a superheated high pressure steam. Entrained fly slag and ash are then removed from the partially cooled raw gas using cyclones and filters. The gas is then cooled further and scrubbed of any residual solids in a wet scrubber system. Captured solids are recycled to the gasifier or mixed with the gasifier slag for disposal. The solids free raw gas is then passed over a COS hydrolysis catalyst and subsequently treated with a chemical solvent to remove all sulphur compounds. The clean fuel gas is normally reheated and may be saturated with water before being used in the combustion turbine.

The *Shell* gasifier used as part of the Demkolec project in the Netherlands gasifies about 2500 t/d of coal in a single unit. This is the largest commercial gasifier in the world. The primary objective of this project was to demonstrate a number of factors which are part of the technical risk considerations. This includes the design of the membrane wall and refractory life, syngas cooler design, feeding

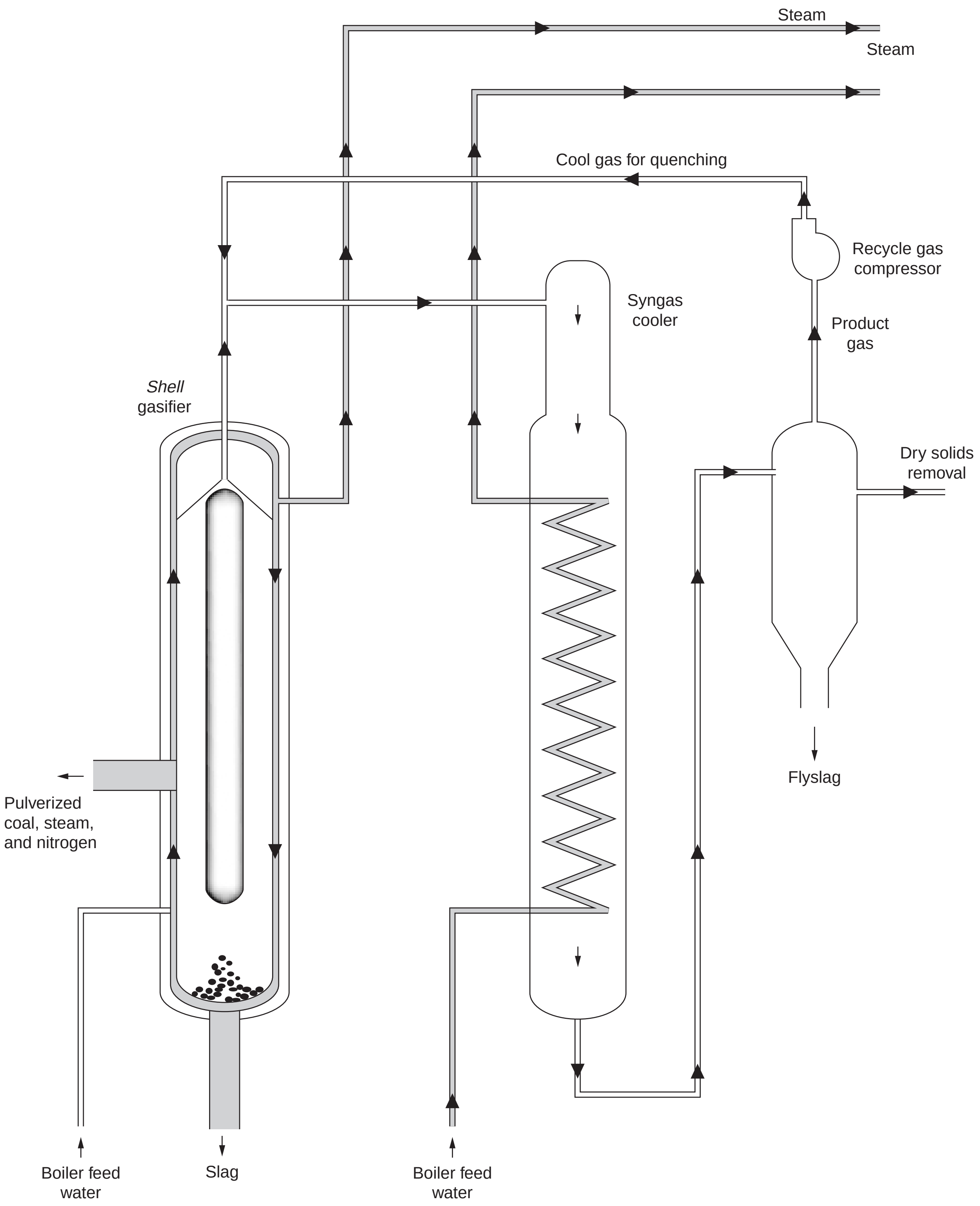

Figure 6

Schematic of *Shell* gasifier with syngas cooler.

reliability, gas recycle reliability and solids collection operability. It appears that all these issues have been resolved during the initial stages on the demonstration.

A high solid feedstock flexibility of this gasifier should be noted. This results from the dry feeding system. Thus, any feedstock which can be pulverized can be readily gasified. With respect to the gasification of petroleum coke, the *Shell* gasifier is perhaps the most suitable, compared with the other gasifiers. However, a low ash content in the coke may require the addition of a mineral matter to the coke to ensure formation of the protective layer of slag on the membrane wall, at least during the initial stages of the operation. A significant modification of the feeding system would be required to enable feeding of vacuum residues and visbreaking tar, as well as that of refinery sludges. However, there are some indications on the *Shell*'s development of an upscaled coannular burner to handle extremly viscous feedstocks such as visbreaking tars.

Prenflo is a dry feed pressurized entrained flow gasifier, a further development of the *Koppers-Totzek* process. Some features of the feeding system and the gasifier are similar as that of the *Shell* gasifier. Dry pulverized feedstock (less than 100 microns) is pneumatically transported with nitrogen to the gasifier where it is gasified with oxygen and steam. The gasifier is lined with water cooled refractory to withstand the temperature of up to 2000°C and has similar features as *Shell* gasifier. Raw gas leaves the gasifier and enters a radiant cooler directly above the gasifier. The radiant boiler has pendent tube walls protruding into the interior of the boiler, forming several flow channels for heat transfer enhancement. The waste heat boiler generates high pressure and intermediate pressure steam to be used in the steam turbine. Two ceramic candle filters are used for the removal of particulates before the gas enters *Venturi* scrubber to remove chlorine and alkalis from the gas. Separated particulates are recycled directly to the burner of the gasifier.

The IGCC plant employing the *Prenflo* gasifier is now under construction in Puertollano Spain as part of the *Elcogas* project. The throughput of the gasifier is similar as that of the *Shell* gasifier used in the *Demkolec* project. The primary feedstock will be the 50/50 blend of the petroleum coke supplied from the adjacent refinery and a high ash (about 45%) local raw coal. Similarly as in the case of the *Shell* gasifier, all kinds of solid feedstocks can be gasified. It is indicated that future testing will verify the use of liquid fuels, principally low value waste streams. With this option available, suitability of the *Prenflo* gasifier for integration with a refinery can be significantly enhanced.

4.3 Other Entrained Bed Gasifiers

It is again emphasized that entrained flow gasifiers are gasifiers of the choice for refinery residues as supported by the available information. There are at least two other commercial entrained flow gasifiers, i.e., air blown gasifier developed in Japan by CRIEPI and the GSP gasifier developed in Germany. The former employs two stage reactor and dry feeding system. The GSP gasifier has similar features as *Shell* gasifier. There is no information in the literature indicating the use of these entrained flow systems for gasification of refinery residues.

5 DESCRIPTION OF IGCC PLANT

An overall block flow diagram of an IGCC plant employing the *Texaco* gasifier is shown in Figure 2. The plant consists of several major sections, i.e., feedstock preparation, gasification, gas clean-up, sulphur recovery, heat recovery, turbines and water treatment. In view of the above discussion, the description of the plant will consider the gasifiers such as *Texaco, Shell* and *Prenflo*. The operating characteristics of these gasifiers are given in Table 12. Thus, little information is available on the commercial gasification of refinery residues using the other gasfiers. A common feature of these gasifiers are high temperatures (approaching 1500°C) which ensure high gasification rates. The plant layout shown in Figure 2 considers electricity as the only final product, i.e., the full heat recovery option.

TABLE 12

Operating characteristics of entrained flow gasifiers

	Prenflo	*Shell*	*Texaco*
No. of gasifiers	1	1	1
Feed type	Dry pulverized	Dry pulverized	Slurry
Feeding system	Lockhopper pneum.	Lockhopper pneum.	Pumping
Exit temp. (°C)	1500-2000	1500-2000	1260-1540
Carbon conv.(%)	99.5	99.5	98-99
Gasifier lining	Water wall refrac.	Water wall refrac.	Refractory
Temp. to SGC (°C)	900	900	900
Rad. SGC* location	Above	Above	Bellow
Rad. SGC design	Water tube	Water tube	Water tube
Convection SGC	Water tube	Water tube	Water tube
Dry partic. system	Cyclone/filter	Cyclone/filter	Water scrubbing
Solid waste	Slag	Slag	Slag

* SGC: syngas cooler.

5.1 Full Heat Recovery Option without Coproduction

In this case, all synthesis gas produced and heat recovered are used for the production of elctricity. With this option, the overall thermal efficiency of the power generation via IGCC exceeds 40%. This represents a decrease in CO_2 emissions per unit of the electricity generated besides the decrease in the other emissions as indicated in Table 1.

Preparation of the solid feedstock in the first step is influenced by the feeding system employed. A wet grinding is used for the slurry feeding system. The wet grinding has some safety advantages over the dry grinding. Also, an oil contaminated water and/or sludges can be added already during the slurry preparation stage. The dry grinding is performed under the blanket of nitrogen. The overall water requirements of the plant are significantly lower in the case of a dry feeding system. In some cases, this fact may influence the choice of the gasifier. Specially designed nozzles and pumps are used for the injection of the liquid and molten feedstocks, wehreas the lockhopper systems are used for the dry feeding.

A common feature of the entrained bed gasifiers are high tempereatures which ensure high gasification rates. The heat recovery systems around the gasifier represent the major difference among the *Texaco*, *Shell* and *Prenflo* gasifiers. In the full heat recovery mode, the *Texaco* system employs a radiant and convective cooler which generate a high pressure steam. In the case of the *Shell* gasifier, the gasifier products approaching 1500°C are quenched by a recycled gas to about 900°C before entering the syngas cooler to generate a high pressure steam in addition to the high pressure steam generated in the reactor membrane walls. For the *Prenflo* system, a radiant cooler comprising suspended tubes is placed on the top of the gasification section. In the full heat recovery mode, only *Shell* gasifier employs a direct quench of the hot gasifier products. It appears that the *Prenflo* system may achieve a higher thermal efficiency than the *Texaco* and *Shell* gasifiers because of the direct heat recovery from the hot gasifier products. In the *Texaco* gasifier, the heat is recovered in the radiant cooler as well, however, part of the heat is lost due to the evaporation of the slurry water. The different features of the gasifiers suggest the different requirements on the material. For example, the suspended tubes in the *Prenflo* radiant boiler will be exposed to much more corrosive and erosive atmosphere than the tubes in the syngas cooler of the *Shell* system. Therefore, the long run performance of the *Prenflo* gasifier on a large commercial scale still has to be demonstrated. In this regard, most of the commercial experience has been gained with the *Texaco* and *Destec* gasifiers, however, the *Shell* gasifier may soon reach the same level of confidence assuming that all phases of the *Shell* process demonstration as part of the *Demkolec* project are successfully completed.

The raw gas leaving the high temperature heat recovery unit contains a small amount of particulates which are removed in the particulate removal system such as cyclones and filters. *Shell* and *Prenflo* have successfully tested ceramic filters on a near commercial scale. The fly slag can be recycled back to the gasifier or conveyed to a fly slag lock-hopper. After purging with a high pressure nitrogen, the lock-hopper is depressurized and the fly slag conveyed to the storage. In the case of *Texaco* gasifier, the raw gas from the syngas coolers is water washed in the carbon scrubber to produce a particulate free saturated gas. The particulate free syngas enters sulfur removal units discussed above.

Before utilized in the combustion turbine, the clean gas after exiting the acid gas removing unit is moisturized to reduce NO_x formation. The gas turbine is equipped with the heat recovery steam generators to recover waste heat from the combustion gases. High, intermediate and low pressure steam is produced. In addition, similar kinds of steam generated in the gasification plant, i.e., high pressure steam produced in the reactor's walls (*Shell* and *Prenflo*) and radiant cooler (*Texaco*) as well as in the syngas cooler, intermediate pressure steam produced by further cooling of the gasifier products as well as from the Claus waste heat boiler and low pressure steam. All high pressure steam is utilized in the steam turbines. Part of the intermediate pressure steam can also be used in the steam turbine while the rest is used for heaters in the gasification plant and other parts of the petroleum refinery. All low pressure steam requirements in the gasification plant are supplied from the combined cycle.

5.2 Partial Heat Recovery and Coproduction

In this configuration, part of the steam recovered from the heat recovery steam generators and/or part of the synthesis gas is used to produce other final products. The former may be used to satisfy requirements of the petroleum refinery or sold to an adjacent industry. Also, in a site specific case, steam can be used for the district heating. The direct quench mode of the *Texaco* gasifier is ususally chosen when coproduction is equally or more important than electricity generation. In this case, after being quenched, the gas is saturated with steam required for the water-gas shift reaction to adjust H_2/CO ratio for the subsequent synthesis. If H_2 is the final product, the water-gas shift is performed in several steps. The product of every step enters the CO_2 scrubber. In a specific situation, CO_2 can be used, e.g., for the enhanced oil recovery. There could be some other options for the utilization of CO_2 [29].

Conversion of the synthesis gas to fuels is commercially proven. Thus, one commercial plant in Sasol in South Africa has been producing transportation fuels for many years, while the other at Great Plains, United States, produced the synthetic natural gas. Of course, viability of these routes is dictated by the economics which are today unattractive. There are several commercial plants in the world producing ammonia from the synthesis gas made by gasification. Also, the commercial plant operated by the *Tennessee Valey Authority* in United States has been producing oxyganets for several years. Studies are in the advanced stages, to evaluate synthesis gas for the direct reduction of iron ore [30]. This suggests that there is a potential for the integration of the gasification technology with petroleum refinery and steelmaking. There are several commercial *Texaco* gasifiers in operation in China using refinery residues as feedstocks, producing ammonia and chemicals as final products [31].

6 INTEGRATION OF PETROLEUM REFINERY WITH IGCC PLANT

The addition of the gasification process to the petroleum refinery does not require significant modification of the refining cycle. Thus, the gasifier only marginally influences the conventional refinery configuration by being positioned in a cascade with upgrading processes such as visbreaking, coking and deasphalting. At the same time, the electricity generated can have a significant impact on the refinery product mix. Besides electricity, hydrogen can be produced for the refinery requirements. Most of the units down stream gasifier, i.e., gas clean-up, Claus plant, heat recovery systems, steam and gas turbines, etc. are part of a typical refinery operation. It is emphasized that power generation within a refinery is not a new activity and is in reality widely practiced. However, refinery power plants usually supply power only for internal consumption. With the development of IGCC plants, only a small fraction of the power generated by the refinery will be consumed internally with the rest being sold to the external consumers. The revenues from the sale of electricity can have a significant impact in economic terms. In a medium sized refinery (10 Mt/y) operating a visbreaker, this can represent over 30% of the total refinery income if all of the visbreaking tar is used for electricity generation [32].

In most cases, the environmental factors appear to be the driving force behind installing a gasification plant on the refinery site. However, it may be worthwhile to evaluate the integration from the point of view of the economic benefits as well. The integration scheme for any new grassroots refinery will depend on the crude charged and available markets for electricity, vacuum pitch, coke and liquid fuels. For existing refineries, capacities and the potential of debottlenecking these units may be an important consideration in selecting the optimal scheme. Nevertheless, the addition of an upgrading unit and a gasifier to the refinery ensures more efficient processing of crude oil and the flexibility to meet the changing demand patterns and fuel quality specifications.

A general analysis of several cases published by Iqbal *et al.* [33] showed that bottom upgrading adds substantial value to the operating economics of a refinery. For example, the cash operating margin per barrel of crude charge to the refinery improved significantly, as shown in Table 13. The most significant increase in operating margin was achieved between the base case and the base + deasphalting + gasifier case. As expected, the annual cash operating margin, defined as positive cash flow in thousands of dollars per year per million dollars of capital investment, as well as the gain in operating margin on per million dollars of additional investment for base case, have also increased significantly (Table 14). All these estimates (Tables 13 and 14) are in second quarter 1995 dollars. This brief overview indicates a great potential for the integration of petroleum refinery with the gasification of the final residues. In addition, the environmental problems with the residues are solved as well.

TABLE 13

Cash operating margins for different integrations [33]

Refinery configuration	Operating margin ($/bbl)
Base	1.52
Base + coker	3.05
Base + coker + gasifier	4.35
Base + deasphalting	3.32
Base + deasphalting + gasifier	6.30

TABLE 14

Annual cash operating margins and margin improvement [33]

Refinery configuration	Annual cash operat margin (M$/y/M$ cap. inv.)	Margin improvement (M$/y/MM$ of increm. inv.)	Investment (MM$)
Base	59.70	0.00	1061
Base + coking	86.86	158.71	1462
Base + coking + gasifier	94.40	137.35	1918
Base + deasphalting	103.47	271.72	1337
Base + deasphalting + gasifier	130.19	208.74	2013

The information in Tables 13 and 14 is the only information of its kind found in the literature, therefore, a more detailed description of the cases appears to be desirable. In the base case configuration the vacuum residue is not processed further, but it is blended with FCC slurry oil and cycle oil to produce a 4% sulphur heavy fuel oil. The vacuum tower design achieves a vacuum gas oil cut of 1075°F (580°C) to minimize residue production.

The flowsheet for the case involving base case + coker + gasification is shown in Figure 7. The study assumes the processing of 120 000 bpd of a Venezuelan crude. At first, only base case + coker will be examined. In this case, the vacuum residue is upgraded in a delayed coker to give liquid products and petroleum coke. The intermediate liquid

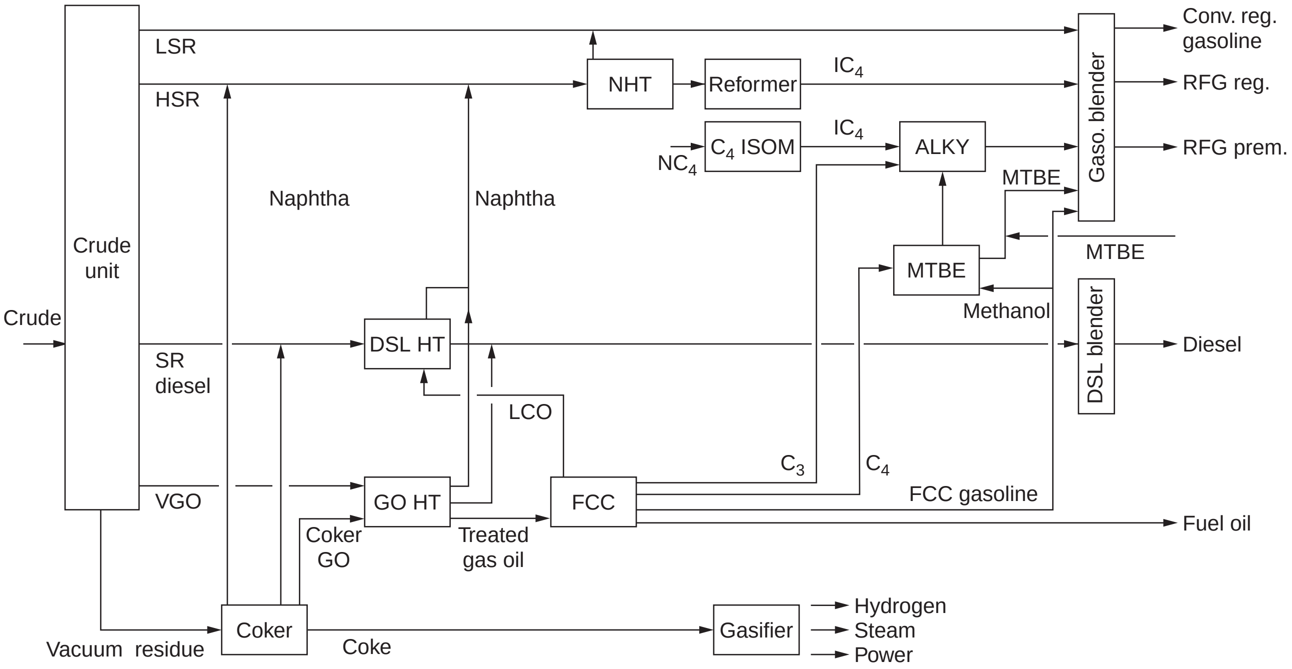

Figure 7

Refinery with coker, LSR-light straight run naphtha, HSR-heavy straight run naphtha, SR diesel-straight run diesel, VGO-vacuum gas oil, coker GO-coker gas oil, GOHT-gas oil hydrotreater, LCO-light cycle oil, DSLHT-diesel hydrotreater, NC_4-normal butane-IC_4-iso butane, MTBE-esterification unit, C_3-propane/propene mixture from FCC, C_4-butane/butene mixture from FCC, RFG reg-regular grade reformulated gasoline, RFG prem-premium grade reformulated gasoline, gaso-gasoline, DSL-diesel, FCC-fluid catalytic cracking unit, NHT-naphtha, C_4 ISOM-butane, isomerization unit, ALKY-alkylation unit [33].

streams from the coker are hydrotreated in a similar way as in the base case. These products add to the total amount of products available for sale. The steam and hydrogen required for the coker and additional hydrotreatment are generated within the plant, whereas electricity is purchased from outside. When a gasifier is added, problems with petroleum coke, i.e., storage, handling, marketing, etc. are eliminated. The coke is converted to syngas containing mainly CO and H_2. After cooling and desulphurization, the syngas is steam reformed to yield a mixture of H_2 and CO_2. High purity H_2 is recovered by pressure swing adsorption for use in the refinery. The remainder of the syngas is combusted in a turbine to generate power. High pressure steam is generated by cooling the gas turbine exhaust. This steam is expanded in a steam turbine to generate additional power and the lower pressure steam is used in the refinery.

The addition of deasphalting and a gasifier to the base case requires a slight modification of the flowsheet (Fig. 8). At first, butane is used to split the residue into the deasphalted oil (DAO) and asphaltenes. The conditions are selected to ensure that the amount of metals in DAO oil is low for smooth hydrotreatment and subsequent FCC of DAO. Also in this case, steam and hydrogen are generated internally and power purchased from outside. When the gasifier is added, the asphaltenes are converted to syngas, similarly as in the case of petroleum coke. If the asphaltene production is higher than that of coke (e.g., because of DAO quality requirements), the gasifier capacity is higher, i.e., more power is generated for export compared with the coke case. On the other hand, in some cases, it may be possible to choose the operating conditions of the deasphalting unit to produce more DAO and less asphaltenes and correspondingly higher liquid yields than a coker operating on the same feed. It appears that the integration analysis published by Iqbal *et al.* [33] assumes a generic type of delayed coker and *Shell* gasification process (SGP), whereas the Residual oil supercritical extraction (Rose) process was chosen for the deasphalting unit. The visbreaking case was not included.

In a similar study, Quintana and Falsetti [34] used a *Texaco* gasifier for processing a 565°C vacuum residue derived from the Mayan crude, i.e., the total refinery capacity was 22 000 t/d producing 8100 t/d of the residue. The residue was further treated by either deasphalting (Rose) or delayed coking. Some parameters estimated in this study are shown in Table 15.

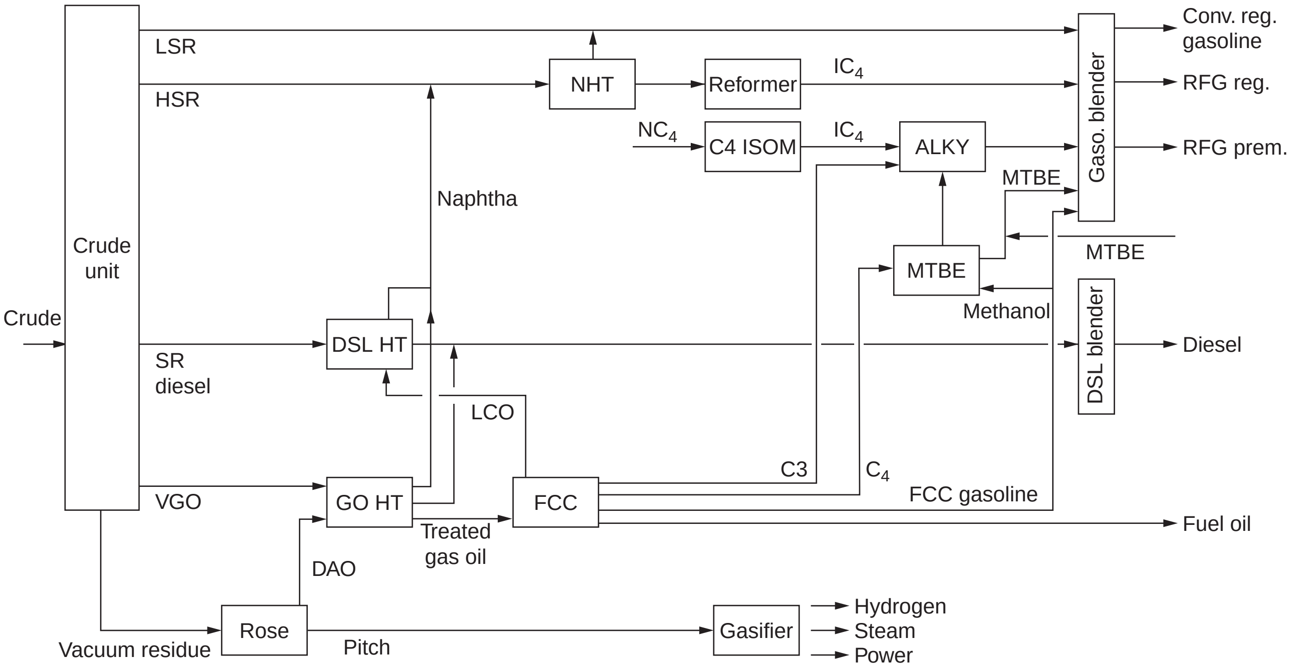

Figure 8

Refinery with solvent deasphalting, Rose-residue oil supercritical extraction unit, DAO deasphalted oil, other abbreviations as in Figure 7 [33].

TABLE 15

Some parameters from integration of *Texaco* gasifier [34]

Parameter	Deasphalting	Delayed coking
Upgrading		
Conversion (%)	40	37
Yield (t/d)	4800	3000
Gasification		
Feed rate	1500	2000
Sulphur (wt.%)	6.9	7.1
HHV (Kcal/kg)	9600	8300
Hydrogen, 1000 Nm^3/h	90	90
Electricity (MW net)	80	80
Steam	*	*
Capital (US$MM)	180	210
Additional feed	3300	1000
Equiv. add. power (MW)	530	135

Both the deasphalted oil and liquid products from delayed coking were hydrotreated using a T-Star process. The visbreaking case was not included in this analysis. In the following, the commercial projects in United States and Europe will be discussed in more details.

6.1 Commercial Projects in United States

The El Dorado *Texaco* project is a unique case of installing a relatively small gasification unit to obtain economic benefits and to solve environmental problems in a refinery. At the present time, the El Dorado refinery in Kansas, United States, is a 100 000 bbl/d complex comprising crude and vacuum distillation units, isomerization, alkylation, reforming, FCC, delayed coking, hydrotreating, H_2 production, gas liquefaction and distillation, sulphur recovery, aromatics complex, phenol and acetone production [8]. The flowsheet of the refinery is shown in Figure 9. The project team has evaluated several options to meet the refinery's utility requirements in compliance with environmental regulations, i.e., both the economic and regulatory pressures being imposed on refiners were taken into consideration. The gasification power plant offered a number of benefits over the other alternatives. The nominal rating of the plant is 40 MW and the turbine's exhaust heat produces about 180 000 lb/h of 600 psi and 150 psi of superheated steam. It meets all of the refinery's power requirements and 40% of its steam needs. The gasifier enabled the refinery to shut down one of its fired boiler which was used for steam production. The unit was sized to utilize the excess coke (about 120 t/d). Thus, inspite of its small size, the unit is not considered to be a demonstration unit for the *Texaco* process but rather a

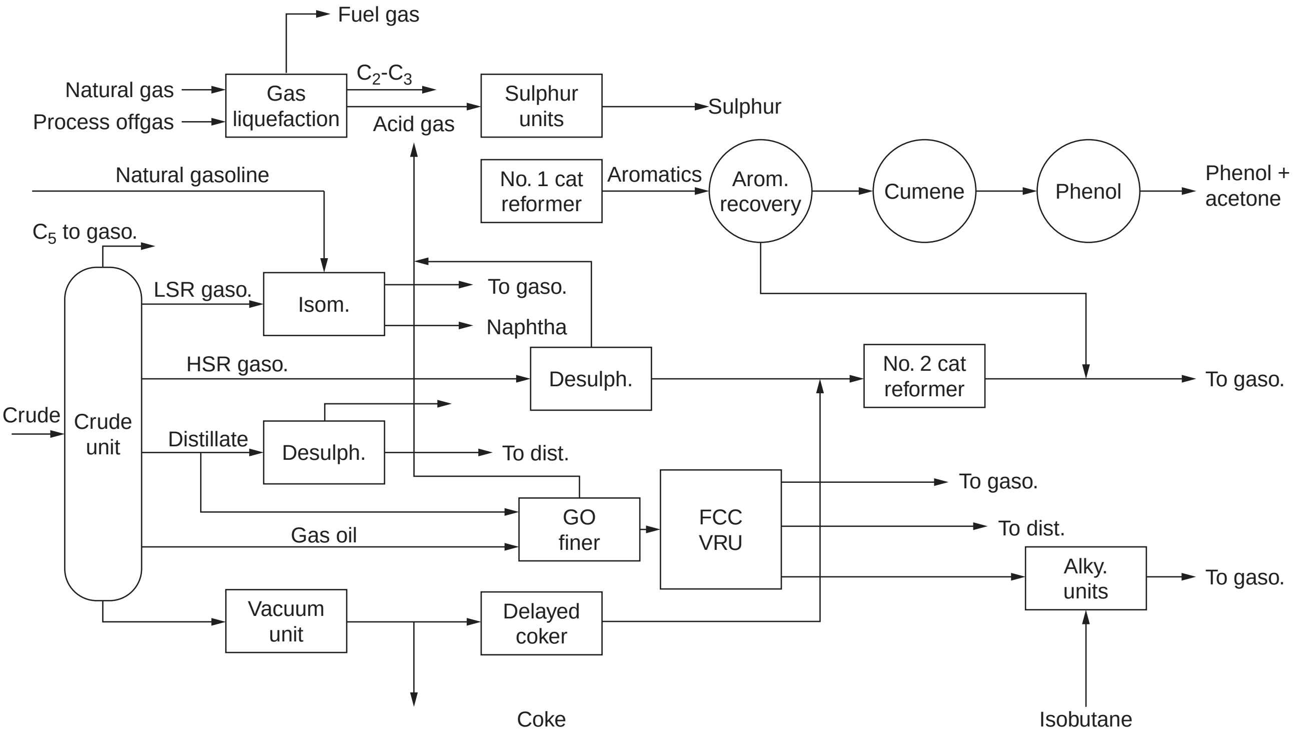

Figure 9

Flowsheet of El Dorado refinery.

---

commercial unit. A combination of various economic and environmental factors showed that the direct quench mode of the *Texaco* gasifier was the most suitable for the plant. The duration of the project, starting with the detailed enigineering work and ending with the start-up was about two years at a total cost of $80 million.

Significant reductions of SO_x and NO_x emissions was achieved by replacing the previously performed offsite combustion of 120 t/d coke by gasification. In addition, four other streams of refinery wastes (Table 16) totaling about 10 t/d are being incinerated in accordance with EPA regulations. Also, a theoretical decrease in emissions is associated with the power which the local utility is no longer generating for refinery usage. Other important environmental factors relevant to the project were discussed in the Introduction.

The addition of the gasification plant resulted in significant economic benefits. Previously, the refinery was spending $12 to 14 M/y on power purchases from the local utility. The refinery now pays only a few million dollars a year for stand-by services. In addition, the refinery is saving about $1 M/y in waste shipment and disposal and almost $1 M in nitrogen costs. Steam production costs have been reduced by more than half. Other benefits result from oxygen enrichment of the sulphur plant which will enable the refinery to process a wider range of high sulphur crudes when the sweet/sour differential becomes attractive.

A new petroleum coke gasification plant at the *Star Enterprise* refinery at Delawere City will gasify more 2000 t/d of fluid coke to generate 225 MW electricity. Another plant is being considered by *Koch Ref. Co.* This plant will convert a low value, high sulphur petroleum coke to power, hydrogen and steam.

TABLE 16

Gasifier feeds in El Dorado refinery [8]

1	Petroleum coke
2	API separator bottom designated as K051 waste (75% water; dry portion is composed of 60% ash, 35% carbon and small amount of hydrogen, sulphur and nitrogen)
3	Acid soluble oil (ASO) from alkylation unit designated as D001 or D018 waste
4	Primary waste water treatment sludge classified as F037 and F038 waste
5	Phenolic residue (tower bottoms from the phenol production unit)

6.2 Projects in Italy

There are several IGCC projects in Italy, each at a different stage [35]. All are planned to be constructed in refineries and to use heavy residues as feedstock. Italy has suddenly become the cutting edge of this technology in refineries for residue disposal. These projects represent an attempt by refineries to enter the fastest growing and perhaps the most profitable energy business of future-electricity [36].

There are several factors favoring the integration of IGCC technology with petroleum refineries in Italy. First of all, the refining industry in Italy is characterized by widespread use of visbreaking processes. Thus, among 18 refineries in operation, 11 have visbreaking plants giving a total conversion capacity of almost 20 Mt/y [32]. This represents a visbreaking tar availability of about 8 Mt/y from which it would be possible to obtain almost 4400 MW of electricity. Currently, the tar is used to produce a high sulphur heavy oil (HSHO) by blending it with heavy gas oil in about 70/30 ratio (tar/gas oil). The disposal of the tar via gasification frees up the gas oil which may be used to produce transportation fuels. An IGCC plant of 500 MW will consume about 1 Mt/y of tar. The diluent distillate freed up in this case is around 400 000 t/y [36]. It is evident from the simplified flowsheet of IGCC integration with the visbreaker that streams leading to the HSHO can be eliminated.

Meeting environmental standards is another driving force for implementing IGCC technology in Italy. In particular, the limits set by the EC Large Combustion Plant Directive for new large plants have been extended to the existing plants. This will result in a significant decline in the consumption of HSHO in Italy, using conventional methods. Because of its environmental benefit in disposing of the visbreaking tar, the production of electricity via IGCC in refineries is eligible for subsidies. In 1994, the price of electricity was fixed at 130 lires/kWh of which 50 lires represented subsidies. The price is guaranteed in the first 8 years of investment and then revised according to inflation. Also, the quantities of electricity are supplied to Italian electric utilities according to a long term commitment.

The change of product slate which results from a change in the refinery configuration is shown in Table 17 for a typical medium size (10 Mt/y) Italian refinery operating a visbreaker [32]. The refinery has an internal consumption of about 30 MW. If only 75% of the visbreaking tar produced is gasified, the refinery power consumption represents only 6% of the total power capacity installed (about 500 MW).

The construction of a 512 MW IGCC plant is underway on the site of the *Isab* refinery located in Priolo Gargallo near Siracusa in Sicily [37]. The plant is constructed by a consortium of *Snamprogeti* and *Foster Wheeler Italiana* under a $730 million lump sum turn key contract. Commercial operation is planned for November 1999. The visbreaking tar will be gasified to produce steam and hydrogen for internal refinery consumption. a high purity sulphur will be sold to agricultural and chemical industries. The Italian power utility (*Enel*) will purchase electricity under a long term purchase agreement. *Edison Mission Energy*, subsidiary of *Edison International* owns 49% of the project and *ERG Petroli*, owner of the *Isab* refinery owns 51%.

TABLE 17

Refinery output (wt.%) for Arabian light crude [33]

Products	Refinery configurations			
	A Basic	B Convent. upgraded	C Deeply upgraded	D B + IGCC
Light distillates	19	32	39	32
Middle distillates	33	41	42	46
Heavy products	45	21	10	6
IGCC charge	-	-	-	10
Self consump. + losses	3	6	9	6
Total	100	100	100	100

Explanation to refinery configurations:
A: Atm. and vac. distillation + reforming + HDS of middle distillates;
B: A + cat. cracking + visbreaking + deasphalting + alkylation + dimerization;
C: B + hydrocracking + deasphalting + HDS of DAO;
D: C + IGCC (charge corresponds approximately to 500 MW).

Edison International led the development of a 100 MW Cool Water plant the first near commercial IGCC plant, in Southern California.

A 276 MW *Anonima Petroli Italiana* (*API*) project located at Falconara, will gasify 7700 bbl/d of visbreaking tar to produce electric power for sale to a local utility [38]. In addition, steam will be produced for internal refinery consumption and a high purity sulphur for export. The ownership of the plant includes *API* [51%] and *ABB* (25%) with *Morgan Stanley* being the financial adviser. *Saras* project, scheduled for commercial operation in 1999, will be the world's largest IGCC plant at 550 MW. The plant will be constructed at the *Saras Oil Refinery* in Sarroch, Sardinia [39, 40]. A consortium including *Nuovo Pignone* (80% owned by General Electric), *Turbotechnica* and *Snamprogetti* was selected as the turnkey supplier for the project by *Sarlux*, a joint venture between *Saras* and *Enron.*

6.3 Other Projects

The *Shell* plant at Pernis, The Netherlands, will gasify tar from a vacuum residue visbreaker [2]. The gasifier will be supplied by *Shell* Lurgi. The plant comprises three *Shell* gasifier parallel trains with 550 t/d capacity each. The so-called trigeneration plant will produce power with cogenerated heat and synthesis gas for high value chemicals [41]. H_2 will be used in a new hydrocracker which is an integral part of the project. The remainder of the syngas will be used for power generation (approximately 80 MW) most of which will be sold to the national grid. Medium and low pressure steam will be produced as required by the refinery. Three less efficient and less environmentally friendly boilers will be phased out. Commercial operation on syngas is scheduled for 1997.

A 300 MW (net) IGCC plant is being commissioned at Puertollano, Spain, about 200 km south of Madrid, at an elevation of approximately 700 m above see level [42]. The plant is being built by *Elcogas*, a consortium of the leading European utilities from Spain, France, England, Portugal and Italy. The feedstock for the plant is a 50/50 mixture of petroleum coke and lignite containing about 45% ash. The coke will be supplied from the *Repsol* refinery located about 1 km from the power plant and the coal mine which is approximately 6 km from the plant. About 2600 t/d of the mixture will be gasified. The highly integrated IGCC system with separate generators for the gas and the steam turbine, was selected where the total air for the air separation unit is delivered from the air compressor of the gas turbine. The primary objective of the plant is to demonstrate its high thermal efficiency, i.e., an overall thermal efficiency of 45% is being projected. About 77 t/d of flake sulphur is available for sale. It is projected that the environmental emissions from the IGCC plant will be far below the current European standards. According to the most recent information [43], *Total*, *Électricité de France* (*EdF*) and *Texaco* have launched a joint project to build an IGCC plant next to *Total*'s 320 000 bbl/d refinery in Normandy, France. Feedstocks will include a high-sulfur heavy oil, used lube oil, petroleum coke, and various refinery wastes. About 20% of the 365 MW of electric power produced by the IGCC plant will be for *Total*'s onsite operation, whereas the remaining 80% will be sold to *EdF*. It is projected that the plant will be on stream in 2003 at the estimated total cost of about FF 4 billion.

REFERENCES

1 Tamburrano, F. (1994) Disposal of Heavy Oil Residues, Part 1. *Hydroc. Proc.*, **79**.

2 Tamburrano, F. (1994) Disposal of Heavy Oil Residues. Part 2. *Hydroc. Proc.*, **77**.

3 Mahagaokar, U., Hauser, N. and Creme, G.A. (1993) Gasification of Petroleum Coke in the *Shell* Coal Gasification Process. *Petroleum Coke as a Utility Fuel, EPRI Workshop*, Ft. Lauderdal, Fla.

4 Furimsky, E. (1996) Spent Refinery Catalysts. Environment, Safety and Utilization. *Catal. Today*, **30**, 223.

5 Peries, J.P., Renard, P., Des Courieres, T. and Rossarie, J. (1988) ASVAHL New Routes for Processing Heavy Oils. *4th UNITAR/UNDP Intern. Conf. on Heavy Crudes and Tar Sands*, Edmonton Canada, **2**, Paper no.95.

6 Elliot, J.D., Godino, R.L. and McGrath, M.J. (1985) Noncatalytic Heavy Crude Upgrading. *3rd UNITAR/UNDP Intern. Conf. on Heavy Crude and Tar Sands*, Long Beach, CA, **3**, 1698.

7 Geosits, R.F. and Mohammed-Zadeh, Y. (1993) Coke Gasification Power Generation: Options and Economics. *Power Gen., Americas 93*, Dallas, TX.

8 Rhodes, A.K. (1996) Kansas Refinery Starts up Coke Gasification Unit. *Oil & Gas J.*

9 Clarke, L.B. (1991) Management of By-Products from IGCC Power Generation. *IEA Coal Research*, *Report IEACR/38*, London, UK.

10 Kristiansen, A. (1996) Understanding Coal Gasification. *IEA Coal Research, Report IEACR/86*, London, UK.

11 Takematsu, T. and Maude, C. (1991) *IEA Coal Research*, *Report IEACR/37*, London, UK.

12 McKetta, J.J. (1992) *Petroleum Processing Handbook*. Marcel Dekker, New York.

13 Murphy, J.R., Whittington, E.L. and Chang, C.P. (1979) Review Ways to Upgrade Residues. *Hydroc. Proc.*, **58**, 9, 119.

14 Speight, J.G. (1991) *Chemistry and Technology of Petroleum*. Second Ed., Marcel Dekker, New York.

15 Hamilton, G.L., Fitzgerald, M. and D'Amico, V. (1986) Retrofitting Heavy Oil Processes. *Proc. AIChE Meeting*, Miami, Florida.

16 Schulman, B.L. and Dickenson, R.L. Upgrading Heavy Crudes: a Wide Range of Excellent Technologies Now Available. *5th UNITAR/UNDP Intern. Conf. on Heavy Crude and Tar Sands*, **4**, Caracas, Venezuela.

17 Anon. (1996) Bottom of Barrel Processing Capacity Forecast to Grow Vigorously. *Hydroc. Proc.*, **23**.

18 Washimi, K., Wada, T., Nelson, S., Limer, H. and Schutter, H. (1985) High Conversion Upgrading of Extra-Heavy Oils by a New Process Combination. *3rd UNITAR/UNDP Intern. Conf. of Heavy Crude and Tar Sands*, Long Beach, CA.

19 Bryers, R.W. (1995) Utilization of Petroleum Coke and Petroleum Coke/coals Blends as a Means of Steam Raising. *Fuel Proc. Technol.*, **44**, 121.

20 Child, E.T., Muenger, J.R. and Schlinger, W.G. *Gasification of Oils, Pitch, Coke and Coal Using the Texaco Gasification Process.*

21 Podar, S.K., Ragsdale, R., Geosits, R.F., Hood, R.L. and Lynch, K.Z. (1994) Rose Asphaltenes, a Fuel of the Future. *NPRA Annual Meeting*, San Antonio, TX.

22 Nelson, S.R. and Corbet, R.W. (1985) Ferr-McGee's ROSE Process Expands on Proven Extraction Technology. *UNITAR/UNDP 3rd Intern. Conf. of Heavy Crude and Tar Sands*, Long Beach, CA.

23 Kanakamadela, R.D. and Islam, M.R. (1995) A New Method of Petroleum Sludge Disposal and Utilization. *6th UNITAR/UNDP Intern. Conf. on Heacy Crude and Tar Sands*, Houston, TX.

24 Falsetti, J.S. and Skarbek, R.L. (1993) Petroleum Coke Utilization with *Texaco* Gasification Process. *NPRA Annual Meeting*, San Antonio, TX.

25 Furimsky, E. (1998) Gasification of Oil Sand Coke. Review. *Fuel Proc. Technol.*, 56, 263.

26 Scott, D.H. and Carpenter, A.M. (1996) Advanced Power Systems and Coal quality. *IEA Coal Research Report IEACR/87*, London, UK.

27 Texaco Dev. Corp., Texaco Coal Gasification Process. *Report no. 9-83*.

28 EPRI (1989) DOW Entrained Flow Gasification Process. *RP 2773-12 Technical Report.*

29 Furimsky, E. (1997) Activity of Spent Hydroprocessing Catalysts and Carbon Supported Catalysts for Conversion of CO_2 and H_2S. *Appl. Catal.,* **156**, 207.

30 Simbeck, D. (1997) Steelmaking, Refinery Operations Seen Benefiting from Gasification Technology. *Technol. Forecasts & Technol. Surveys,* 6.

31 Anon. (1996) Gasification Projects: Expansion Continues. *Adv. Fuel Technol. Newsletter No. 196, Energy Policy,* Publ. McIlvaine Co., 23, **647**, 1995.

32 Gulli, F. (1995) Product and Process Innovation in the Energy Industry: The Development of Integrated Tar Gasification Combined Cycle Plants. *Energy Policy, 23,* **647**.

33 Iqbal, R., Patel, V. and Sloan, H.D. (1995) Process Integration for Resid Upgrading Optimization. *6th UNITAR/UNDP Intern. Conf. on Heavy Crude and Tar Sands*, **10**, Houston, TX.

34 Quintana, M.E. and Falsetti, J.S. (1995) Heavy Oil Upgrading Using an Integrated Gasification Process. *6th UNITAR/UNDP Intern. Conf. on Heavy Crude and Tar Sands*, **10**, 463, Houston, TX.

35 Del Bravo, R., Starace, F., Chellini, I.M. and Chiantone, P.V. (1996) *Oil & Gas J.*, **43**.

36 Tabarelli, D. (1995) Integrated Gasification Combined Cycle in Italy. *Petroleum Review*, **456**.

37 Anon. (1996) Construction Begins on Italian IGCC. *Adv. Fuel Technol. Newsletter*, Publ. McIlvaine Co., Northbrook, IL.

38 Anon. Italian Refinery Adds Power Project. *Oil & Gas J.*

39 McIlvaine, R.W. (1996) Two Landmark IGCC Projects. *Adv. Fuel Technol. Newslett. No. 203*.

40 Aalund, L.R. (1996) Italian Refinery Gasification Project to Make Electricity, Steam and H_2 from Tar. *Oil & Gas J.*, **33**.

41 Zuideveld, P.L. (1997) Refinery Operations Seen Benefiting from Gasification. *Technol. Forecasts & Technol. Surveys*, **7**.

42 Schellberg, W. and Hooper, M. (1996) The Puertollano IGCC Plant with *Prenflo* Technology. *Proc. 13th Annual Intern. Pittsburgh Coal Conf.*, **1**, 427.

43 Anon. (1998) *Oil & Gas J.*, **44**.

Final manuscript received in August 1999