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# Integrating delayed coking process into Nigeria's refinery configuration

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## Abstract

The large availability and economic cost of heavy crude both directly from oil wells and as by-products of crude oil processing calls for methods for its utilization. Delayed coking is one method used for processing and utilization of heavy crude; it is deployed as a unit in refineries. An evaluation of heavy residual oil processing units has been done for Nigerian refineries. Process flow schemes of three Nigerian refinery complexes were carefully analyzed and the yields of coke, gas and liquid products were predicted from the study. The study revealed that Nigeria's refineries were in need of such processes like Delayed coking which is seen to have a lot of advantages in technological, economical and environmental perspectives. The developmental trend in the conceptual planning of the existing refineries in Nigeria is light fuel orientation. The product slates of existing refineries are lacking in heavy products of secondary origin. The uses of Delayed Coking Plant (DCP) and its products in contemporary downstream processing had also been highlighted. Nigeria's emerging metallurgical and electrodes manufacturing industries stand to gain in DCP products, particularly petroleum coke, while the economy will be protected as cash flight through coke import shall be minimized with an introduction of DCP into Nigeria's refining configuration.

**Keywords**. Delayed coking, petroleum coke, residuum, Nigeria's refinery, flexibility.

## Introduction

The complete absence of delayed coking plant in the Nigerian refinery system in the face of a plethora of useful applications of petroleum coke in the energy and metallurgical processing industry, as well as the current trend in the processing industry to place emphasis on environmental protection, waste minimization, a recycle and reuse of waste and transformation to wealth, all point to the fact that petroleum processing industry in Nigeria requires a rethinking and revamp in process layout and design.

The operation of currently three functional refineries in Nigeria leaves no doubt that the various existing processes carry along their residual products. The flow diagrams of the major functional refineries in Nigeria, namely: Port Harcourt Refining Company Ltd (PHRC), Warri Refinery and Petrochemicals Company (WRPC) and Kaduna Refinery and Petrochemicals Co. Ltd, (KRPC) were analyzed in the light of modern plant design concept to evaluate the feedstock base and assess the possibility of integrating into the refinery configuration the Delayed coking plant (DCP). The said plant among other advantages has the main objective of producing the much needed petroleum coke for the metallurgical and anode industry and also give value added liquid products yield, reducing residual waste and conserving the environment. Table 1 shows the types of petroleum cokes and their end uses.

*Table 1. Types of petroleum cokes and their end uses (Dymond,1991)*

| Application | Type of coke | State | End use |
|---|---|---|---|
| Carbon source | Needle | Calcined | Electrode<br>Synthetic graphite |
| | Sponge | Calcined | Aluminum anodes,<br>$TrO_2$ pigments<br>Carbon raiser |
| | Sponge | Green | Silicon carbide, Foundries<br>Coke ovens |
| Fuel use | Sponge | Green lump | Europe/Japan space heating |
| | Sponge | Green | Industrial boilers |
| | Shot | Green | Utilities |
| | Fluid | Green | Cogeneration |
| | Flexicoke | Green | Lime, Cement |

Delayed coking remains the industry's leading economical choice for converting heavy crude into high value products, and choosing the right delayed coking process goes beyond improving the bottom line (Feintuch & Negin, 1981; Wodnik & Hughes, 2005). Using modern technological advances besides processing heavier feedstocks, increased throughput, improved safety, reduced environmental emissions, enhanced reliability, flexibility and overall economics of the DCP are significantly achieved (Maples, 1993). Delayed coking is a high temperature process involving extensive used of direct heat to up-grade products (Chen *et al.,* 2004; Akpabio *et al.*, 2006). As a combined process of severe thermal cracking and condensation reactions, needs to consume a large amount of high-grade energy. Akpabio and Obot (2011) added that delayed coking is one of the major additions and targets for upgrades for the processing of the bottom-of- barrel into lighter products such as gasoline and other distillates. The objective of this work therefore is to highlight and explore the raw materials or feed stock base, and the advantages and technico-economic viability of inculcating delayed coking in the refinery flow scheme of this country Nigeria. Obviously, the

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cracking conditions to be applied and the amount and type of cracked products will depend largely on the type of feedstock, in practice, the feedstock for thermal cracking is a mixture of complex heavy hydrocarbon molecules left over from atmospheric and or vacuum distillation of crude. The nature of these heavy, high molecular weight fractions is extremely complex. Coking is one major application of the thermal cracking process. The delayed coking process was developed to minimize refinery yields of residual liquid products. A total acceptability of almost virtually all forms of residual products namely: mazout and gudron from crude and vacuum distillation units respectively, tar sands, coal tar, shale oil, Thermal cracking residue, pyrolytic residue, as delayed coking feedstock materials generate scientific and technological questions in the Nigeria refining industry flow scheme as to the unavailability of delayed coking.

## Methodology

Process flow schemes of the three functional refinery complexes in Nigeria (PHRC, WRPC, KRPC) were carefully analyzed. The treatment patterns of heavy residual products of these refineries had earlier been analysed and the suitability of the feedstock for Delayed coking process was established (Oboho *et al*., 2000). A comparison of Arabian Crude derived residua was used as a feedstock base compatible with that of Nigerian refineries. Vacuum residue and other asphalteno-resinous materials are the feed stocks in thermal cracking process called delayed coking. This is an open technology which occurs in coke drums slowly as the feedstock leaves heating furnace at temperatures above 550 degrees Centigrade (hence delayed) but it is not used in the Nigerian refining industry. The global trend in refinery revamps program has the following keywords – flexibility to handle the changing supply of crude from light to heavier. Heavy crudes are cheaper than sweet crudes due to their limited processing capacity. Delayed coking is one of the major additions and targets for upgrades for the processing of the bottom-of- barrel into lighter products such as gasoline and other distillates.

## Formation of coke

Formation of coke occurs as a result of a series of condensation reaction which gives products with increasing molecular mass and aromaticity according to the scheme shown below:

$$Hydrocarbons \rightarrow \text{resins} \rightarrow asphaltenes \rightarrow coke$$

Thermal decomposition of asphaltene extracted from crude and their refined products occurred at atmospheric pressure in the stream of inert gas directly with formation of coke without intermediate stage and can be illustrated as:

$$Asphaltene \rightarrow Coke + \text{Light Product}$$

Coke yield depends on aromaticity of asphaltene. For native petroleum, it constitutes 50 to 60% and for more aromatized extracted products of destructive origin it has 75 – 80%. Coke formation from native as well as asphaltene of secondary origin occurs according to chain mechanism which is shown below and discussed widely by Magaril (1985) and Zhorov (1987):

$$A \rightarrow A. + R$$

$$R + A. \rightarrow A. + RH$$

$$A. + A \rightarrow A.A.$$

$$AA'A \rightarrow AA'A.$$

$$AA. \rightarrow M + AA'$$

$$(A')_i A. \rightarrow (A')'_i A$$

$(A'.)_i A.$ _ Inactive radical whose free valency is delocalized or screened by alkyl and other groups

A - asphaltene molecules,

M - molecule of relatively light decomposition product liberated in gaseous phase.

*Table 2. Model reactions of coke formation*

| Reaction No. | Reaction | Coke yield, mass fractions | Type of light end product |
|---|---|---|---|
| 1 | $C_6H_{14} \rightarrow 1.15 C_5H_{12}+0.34CH_{0.8}$ | 0.05 | Alkane |
| 2 | $C_6H_{14} \rightarrow 1.33C_4H_{10}+0.68CH_{0.8}+0.8H_2$ | 0.10 | Alkane |
| 3 | $C_6H_{14} \rightarrow 1.32C_2H_4+3.36CH_{o.8}+3.01H_2$ | 0.50 | Alkene |
| 4 | $C_6H_{14} \rightarrow 0.66C_4H_6+3.36CH_{0.8}+3.68H_2$ | 0.50 | Diene |
| 5 | $C_6H_{12} \rightarrow 1.36C_2H_4+3.28CH_{0.8}+2.97H_2$ | 0.50 | Alkene |
| 6 | $C_6H_6 \rightarrow 1.48C_2H_4+3.04CH_{0.8}+2.82H_2$ | 0.50 | Alkene |

The coefficients v has been rounded off.

Model reactions in Table 2 agree with the chemistry that alkanes would yield lower alkanes on mild cracking, whereas severe cracking in reactions 3-6 (Table 2) with corresponding increase in C : H ratio in the feedstock hexane, hexane and benzene yields higher coke mass and the unsaturates diene and alkenes. The participation of the latter in subsequent reactions increase coke yield the more.

## Predicting coke yield when Conradson Carbon Residue (CCR) is known

The most important parameter in predicting the yield of coke is the CCR (weight percent) in the feed.

A simple correlation for estimating a rough coke yield reported by Gary and Handwerk (1975) is:

$$Coke\ yield\ (wt\ \%) = 1.6 \times wt\ \%\ CCR \quad (1)$$

## Predicting yield of gas and liquid products

The equation used to make estimate of the yield of gas and liquid products as a function of CCR:

$$Gas\ yield\ (wt\ \%) = 7.8 + 0.144\ (wt\ \%) \times CCR \quad (2)$$

$$Naphtha\ \ yield\ (wt\%) = 11.29 + 0.343\,(wt\%) \times CCR$$ (3)

$$Gasoil\ yield\ (wt\%) = 100 - coke\ yield\ (wt\%) - gas\ yield\ (wt\%) - naphtha\ yield$$ (4)

Oboho *et al.* (2000) experimentally established that coking of vacuum residues from KRPC besides the gases and liquid balance yield coke up to 28% and when 40% coke powder is fed to the sample, 33.7% is achieved. The material balance of the coking process illustrated in Table 3 indicates substantial coke yield from PHRC Vacuum distillation unit 26.5% mass and also from KRPC 28.0% mass which processes Heavy Lagomar Crude. From a chemical reaction view point coking is considered as a severe thermal cracking process in which one of the end products is carbon (i.e. coke). The coke formed contains some volatile matter. To eliminate essentially all volatile matter from petroleum coke it must be calcined at approximately 2,000$^o$F to 2,300$^o$F. Minor amounts of hydrogen remain in the coke even after calcining which gives rise to the theory held by some that the coke is actually a polymer.

*Table 3. Material balance of Nigerian refineries residual feed stocks in coking process (Oboho et al., 2000)*

| Characteristics | Yields from various samples, % mass | | |
|---|---|---|---|
| | Vacuum residue from PHRC | Atmospheric residuefrom, PHRC | Vacuum residue fromKRPC |
| Feed | 100 | 100 | 100 |
| Gases and losses | 14 | 9.8 | 9.6 |
| Gasoline | 18.3 | 12.6 | 24.8 |
| Intermediate fraction | 41.2 | 65.6 | 37.6 |
| Coke | 26.5 | 12.0 | 28.0 |

Table 4 shows the products obtained in Kaduna Refinery which was designed primarily to process heavy Lagomar Crude. The plants where these products are processed are light end based. Essentially the products are gases and liquid fuels (gasoline, jet, diesel and residual fuels); no coke is produced. This is clearly evident in Table 5 where the various operating units of the Nigerian refineries are shown as well as their handling capacities. Coke yields from Vacuum residues in PHRC and KRPC constitute about 26.5% and 28% respectively which gives a reliable and quality feedstock for Delayed coking process.

The Nigerian processing route uses a conventional-crude-vacuum flasher scheme coupled with vacuum gas oil (VGO) desulfurization followed by fluid catalytic cracking (FCC). Whether or not an additional investment is justified will depend on the specific set of conditions prevailing for either of our refineries. A typical yield slates for vacuum residuum processing in foreign refineries of Arab Light and Arab Heavy Crudes are shown in Table 6. In this table the Gross coke yields of 26.7wt % and 35.4 wt % from the two Arabian Crudes are comparable to the ones in PHRC and KRPC in Table 3, hence Delayed Coking is aptly recommended to be integrated into our refineries' flow scheme. The two alternative conversion routes for processing a typical Arabian Light atmospheric residue are described as shown in Table 7. Either of these alternatives A or B is well acceptable to Nigeria's refineries, especially KRPC.

*Table 4. KRPC product slate*

| NET PRODUCT | BPCD (Barrel per calendar day) |
|---|---|
| LPG ($C_4$) | 588 |
| LPG ($C_3$) | 2,342 |
| Gasoline Unleaded Premium | 16,838 |
| Gasoline Unleaded Regular | 16,838 |
| Gasoline leaded Regular | 8,420 |
| Jet A Fuel | 11,888 |
| Diesel fuel | 12,880 |
| High Sulfur Residual fuel | 22,090 |

*Table 5.Units of Nigerian refineries*

| Refinery Units | PHRC Capacity (bpd) | WRPC Capacity | KRPC Capacity |
|---|---|---|---|
| Crude Unit | 210,000 | 125,000 | 110,000 |
| Vacuum Unit | 54,000 | 34,200 | 38,200 |
| Catalytic Reformer | 39,000 | 21,000 | 17,500 |
| FCCU | 40,000 | - | 21,000 |
| Kerosene Hydrotreater | 33,000 | 15,800 | 17,500 |
| Naphtha Hydrotreater | - | - | 24,000 |
| LPG unit | - | 6,000 | - |
| Alkylation Unit | 7,020 | 2,850 | - |
| Isomerisation Unit | 3,600 | - | - |

*Table 6. Product yields for resid processing in foreign refineries (Source: Feintuch & Negin, 1981)*

| | Arab light resid | Arab heavy resid |
|---|---|---|
| Component (wt %) | Recycle | Recycle |
| Product gas (C4 minus) | 11.2 | 12.9 |
| Naphtha(C5- 430$^o$F) | 15.3 | 14.4 |
| Light gas oil (430 - 650$^o$ F) | 12.1 | 10.2 |
| Heavy gas oil (650- 975$^o$ F) | 34.7 | 27.1 |
| Bottoms (975 $^o$F - plus) | 0.0 | 0.0 |
| Gross coke | 26.7 | 35.4 |

*Table 7. Alternative conversion routes for residues*

| Designation | Description |
|---|---|
| Alternative A | Vacuum flash, DCP, VGO desulfurization and coker gasoil, FCC |
| Alternative B | Residue desulfurization, vacuum flashing, delayed coking, FCC |

### Petroleum coke and metallurgy

Petroleum coke is produced in refinery coking units where the vacuum distillation residue of crude oils (i.e. asphalt) are thermally cracked and separated into gases, liquids and coke (Royal Dutch & Shell, 1983). Green coke is then calcined in kilns to meet industrial standards of structure, size, volatile content and purity. The calcining kilns are refractory lined cylinders 55 to 65 meters in length and about 3 meters in diameter. As the coke

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moves through the revolving kiln it is progressively heated to about 1300°C. Water and volatiles are driven off and the remaining carbon-rich solid is partially graphitized, producing a structure suited for anode production at aluminium smelters (http.www.cii.com/product cylcle.htm, 2000. Petroleum Coke Production).

More fundamental, though, are the anode needs of the Aluminium Smelting Company of Nigeria (ALSCON), which any one of our refineries could equably fill, obviating its importation. Consequently, the prospects of integrating DCP into the refining configuration of the existing refineries or a grass root refinery with heavy oil processing facilities cannot be far fetched in the light of the array of petroleum coke uses shown below in Table 3 which shows the Petroleum coke type as well as end use application.

## Uses of petroleum coke

Depending on the fundamental type produced and the specific impurity levels present in the final product, petroleum coke is basically used for three types of applications, classified as fuel, electrode and metallurgical. A fourth and relatively new usage classification is gasification.

Use for Gasification: Gasification to low-Btu gas or syngas can be accomplished through the use of partial-oxidation techniques. Low-Btu gas can be used as a fuel gas in the refinery; syngas can be used for the production of methanol. However, in new grassroots refineries a large part of fuel needs can be satisfied by gasification.Bottom–of-the-Barrel processing; although process development do continue, the questions which refiners face in deciding on a specific residual-conversion- processing route are mainly ones of application rather than ones of development. Therefore, one of the basic problems is to provide a processing route which makes optimal use of the available bottom–of-barrel residual conversion processes. These bottom-of-the-barrel processes can be classified into five groups, as follows:1. Separation Processes (viz. Vacuum Distillation, Solvent deasphalting), 2. Carbon-rejection processes (Thermal processing, Visbreaking, Combining visbreaking and thermal cracking), 3. Catalytic conversion (Residue catalytic cracking), 4. Hydrogen-addition processes (Residue hydrocracking), 5. Combined Carbon rejection – hydrogen addition (Thermal hydrocracking).

In this classification, delayed coking can be listed under as a carbon-rejection thermal process considerations including: Properties of the crude oils to be processed, marketing requirements economics, including operating costs, grassroots versus expansion and environmental control requirements. Typically, optimization studies using linear programming techniques are utilized during the investigatory phase prior to deciding on a residual – conversion route.

Delayed coking has been declared the preferred low capex hydrocarbon destruction path and the choice for refinery added value and operational flexibility. At the moment there is 7:1 relationship of refining-to-coking capacity in the USA. The ratio in Nigeria is 4:0 which implies there is a tendency for further designs and construction to ignore the DCP as an economical and promising residue processing route for an emerging economy like ours. With DCP the US has the added advantage of operating at high throughput levels, with a 30- 34 API average gravity crude intake, and still produces only 5% residue fuel yield fuel boasting as the only region with such an operational capability (Guillermo, 2006).

Economic studies by SFA Pacific (2003) have illustrated that Fluid Coking was comparative or even more attractive than Delayed Coking. In general terms the capital costs for Fluid coking are lower than Delayed Coking. SFA Pacific also indicates that fluid coke accounts for approximately 5% of the green petcoke produced world-wide in 2002 (3.4M mt/yr out of 79.5 M mt/yr) (SFA Pacific, 2002). Nigeria unfortunately is not part of this production. Increasing activities in residuum processing with Flexi Coking and Fluid Coking have seen twelve plants in all operational since 1976 in the USA which account for over 500 kBD of residuum processing capacity, approximately 12% of the total world-wide thermal conversion (Dymond, 1991; Hammond et al, 2003).

Since delayed coking enjoys the privilege of the preferred residue upgrading option owing to its maturity, inherent flexibility and the ability to handle the heaviest products, some thoughts have also arose with a misconception that product coke can pose some difficulties in the disposal. Although fuel grade coke is a low value product compared to transportation fuels, there is an active global trade even for high sulphur petroleum coke as coke has a high heat value (20% more than coal), making it a very economical fuel. As for the market situation for petroleum coke, it is expected that it will remain robust as traditional coal-fired power stations can take some petroleum coke as fuel. Phillips (2002) asserts that up to 20% coke can be combusted in traditional coal-fired power station with little or no modifications required. Other aspects of delayed coker which received great attention in recent years are safety and operability, yield flexibility and design and operation of major equipment. This has resulted in the development of automated coke drum unheading devices enabling the operator to carry out decoking procedures from a remote location.

## Conclusion

Delayed Coking Plant has been identified as a powerful missing link in the Nigerian Refinery configuration which needs an urgent consideration if the Refining industry shall remain competitive in this era of ever rising oil prices and the tendency to process heavier

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crudes and increase liquid yields to meet the energy challenges of this era. The metallurgical industry is a new target market which will utilize the various cokes, shot coke, sponge coke and needle coke, depending on the feedstock quality of the DCP. Nigerian Crude also produces residues with compatible characteristics to DCP feedstocks in foreign refineries and should be judiciously and economically utilized. Flexicoking or Fluid Coking can as well be considered provided Nigeria participates in the resid petcoke production. The great opportunity borne by DCP has a lot to offer to Nigerian economy and is recommended that we tap from these enormous resources and intensify our petroleum refining industry.

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