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## Resource Recovery from Crude Oil Sludge Using Solvent Extraction and Delayed Cooking Method

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**ABSTRACT:** *The main objective of this work is to make an economically useful recovery from waste. Crude oil sludge is gotten from the bottom of crude oil storage tank. 100ml (109.2g) of crude oil sludge when treated with 50ml, 100ml, 200ml..... 400 ml of solvent heptane resulted in the formation of three different layers. The first layer contains the solvent and some extracted crude oil in the oil phase. This is distilled to get different hydrocarbon fractions. The second layer is asphaltic residue which when furnace treated and activated or washed and neutralized with inclusion of additives yields activated coke used as adsorbent and newsprint paste respectively. The third layer is the mud or clay which could be furnace treated to produce activated clay. Results show that petroleum coke is best activated at 800°C and the optimal condition for bleaching red palm oil by the adsorbent is at 130°C.*

**KEYWORDS:** resource recovery, crude oil sludge, solvent extraction, delayed cooking method

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### INTRODUCTION

Crude oil sludge is the sludge formation that occurs at the bottom of a storage tank where crude oil is kept. The sludge has the same chemical characteristics as crude oil although it contains more polymeric hydrocarbons and solids like sand and clay "The disposal of this sludge constitutes a nuisance to producers and refiners of crude oil because it is associated with ecological hazards as it is being pumped into rivers or disposed as landfills. It is now necessary to develop ways for resource recovery from crude oil sludge as a lot of money is spent in disposing crude oil sludge.

Record shows that Shell Petroleum (Nig.) Spent close to N7.9m on crude oil sludge waste management in 1997 fiscal year and NNPC spent N10m for similar project for the same fiscal year.

In this project, an economically useful resource, asphaltic sludge is recovered from crude oil. Crude oil sludge analysis shows that it contains about 49.67% carbon W/W and therefore if subjected to delayed coking forms petroleum coke which if activated could be used as an adsorbent

petroleum coke is one of the raw materials to produce activated carbon. Printing ink could also be produced from asphaltic sludge.

This study is based on the beneficiation of crude oil sludge by using solvent de-asphalting, delay-coking and thermal activation methods. The asphaltic sludge gotten from solvent de-asphalting can also be washed with distilled water and with additions of additives for different purpose get printing Ink.

Amoco of the United States of America developed the process whereby carbon could be obtained from waste crude oil sludge by delayed coking after solvent extraction. This carbon is activated to get activated carbon. Amoco has also developed a powdered activated carbon (super active carbon) that has 200 to 400 times greater surface area than the usual grades.

Activated carbon came into prominence through its use as an adsorbent in gas masks in World War I. However, the knowledge that carbon produced by decomposition of wood can remove coloring matter from solution dates to the fifteenth century. Many carbonaceous materials such as petroleum coke in this project may be used for the manufacture of activated carbon but the properties of the finished material are governed not only by the raw material but by the method of activation. Decolorizing activated carbons are usually employed as powder. Thus, the raw materials for this type are either structureless or have a weak structure.

Activated carbon differs from graphite by having a random imperfect structure, which is highly porous over a broad range of pore sizes. Petroleum coke can be activated by treatment with oxidizing gases such as air, steam or carbon dioxide or carbonized in the presence of chemical agents such as zinc chloride or phosphoric acid. Most used is the steam activation method. Activation is a physical change wherein the surface of the carbon is tremendously increased by the removal of hydrocarbons.

Printing Ink is also developed from asphaltic sludge in the crude oil sludge. Printing ink can be defined as a mixture consisting of mainly colorants, which are dispersed, in vehicle with added driers forming a paste, which can be printed on a surface.

Conventionally, printing ink comprises of coloring matter, which may be a pigment or dye, a vehicle, solvents, and some additives. The function of the vehicle is to act as a carrier for the pigment. It equally serves as a binder to affix the pigment to the printing surface. Pigments are solid coloring matter in inks. Its other function is to give the printing ink the required opacity. The solvent wets the surface on which the ink is printed.

This project describes my approach to newsprint paste ink production from asphaltic sludge. The asphaltic sludge constitutes the pigment, and the vehicle is mainly mineral oil. Various additives

were used in prescribed quantities to improve the tackiness, hiding power, drying rate, gloss, and rheological properties.

The experiments carried out showed that highly effective adsorbents for the bleaching of red palm oil could be obtained from thermal activation of asphaltic sludge produced from solvent extraction of crude oil sludge. Although several methods exist for bleaching of palm oil, adsorption is the most advantageous because it results in low oil loss and eliminates pollution problems. This project proves the possibilities of generating local adsorbents and printing ink from waste material.

## LITERATURE REVIEW

### BOTTOM-OF-THE-BARREL PROCESSING

It would be seen that various processes can meet the requirements but to varying degrees. The type of processes applied and the complexity of refineries in various parts of the World are determined largely by the product distribution required. Refiners face problems of application rather than development in deciding on a specific residual-conversion processing route. The relative importance of the processes trends towards increased conversion, better product quality and more rapidly changing product pattern. One of the basic problems is to provide a processing route that makes optimal use of the available bottom-of-the-barrel residual conversion processes. This bottom of the barrel process can be classified into five groups as follows.

1. Separation processes
  - Vacuum distillation
  - Solvent de-asphalting
2. Carbon Rejection process, thermal processing
  - Visbreaking
  - Delayed caking
  - Fluid caking and flexi coking
  - Combination of Visbreaking and thermal cracking
3. Catalytic conversion: Residue catalytic cracking
4. Hydrogen addition processes: Residue hydro cracking
5. Combined Carbon rejection-hydrogen addition: thermal hydrocracking.

### PROCESSES INVOLVED IN BOTTOM-OF-THE-BARREL CONVERSION

There are many processes, which can successfully involve extraction of solvent and carbon rejection. Some of these processes will be described and the most suitable chosen.

## **SOLVENT EXTRACTION PROCESSES**

Solvent extraction process is based on the use of a solvent in which one group of feed components, usually the aromatics, is preferentially dissolved. The choice of solvent depends primarily on its selectivity i.e. its ability to distinguish between two or more chemically different groups of components. It must be cheap and readily available, resistant to chemical change during use, non-corrosive and cheap to handle. Its boiling point must be sufficiently different from that of the feed to be extracted so that recovery of the solvent can be performed by simple distillation or flashing.

In this process, the oil fraction is thoroughly mixed with a solvent and the mixture is allowed to settle, layers or phases are formed depending on the component of the oil fraction. The top phase will contain nearly all the solvents plus the dissolved components (e.g., the aromatics). The other (raffinate) phase will consist of undissolved components (the paraffins) and little solvent. After removal of the raffinate, a raffinate and an extract are obtained which are chemically unchanged.

The quality of the raffinate can be improved by repeated extraction with fresh solvent. In practice, the extraction i.e. performed in a number of stages through which feed and solvent flow counter currently. In this way, the raffinate is treated in the last stage with pure solvent. The feed is first contacted with solvent, which is partly loaded with soluble components. The selectivity of the solvent and its ability to dissolve certain groups of components are influenced by temperature, the temperature range throughout the extraction system is being carefully controlled.

## **FURFURAL PROCESS**

In this process, the refined oil mix (raffinate) contains so little solvent that it can often be purified by heat exchange and steam stripping, but the extract solution requires a pipe-still and atmospheric flashing as well as steam stripping. The furfural H<sub>2</sub>O equilibrium system involves partial insolubility and the formation of a constant-composition, constant boiling-point mixture at 97.9°C. This mixture contains 34 % furfural by weight. At room temperature, this mixture separates into a furfural rich solution containing 96% furfural by weight and a water rich solution 8% furfural. This re-constant boiling mixture automatically separates into two solutions at the top of the furfural fractionator. A higher temperature is more usually maintained at the top than at the bottom of the tower but only a slight enhancement of solvent fractionation is attained thereby.

The quantity of solvent employed also varies, but 10 parts of solvent per part of oil have been used in many operations. Contacting is affected in a counter current flow tower, which may be racked with wood slats. The yield of high viscosity index raffinate varies with the stocks being treated but is about 70% for intermediate base stocks and 95% for paraffin-base stocks. Yields

from naphthenes-base stocks are lower and the viscosity Index is necessarily low. The range of temperature is 150°F to 250°F is usually employed most plants operate at about 200°F.

### **PROPANE PROCESS**

This process involves mixing the oil and propane and allowing the asphalt to settle. The low boiling point of propane facilitates its separation from high boiling oils and refrigeration for dewaxing can be obtained by evaporation of the propane. Propane extracts paraffinic hydrocarbons from oil, or inversely precipitates asphaltic or resinous materials. It is used for dewaxing, and it greatly facilitates treatment with sulphuric acid. A system combining de-asphalting and acid treating in propane solution exists. This plant is used to process heavy mixed base residue.

De-asphalting is applied primarily for the separation of small amounts of dark- colored asphaltic materials and thus may or may not result in an oil product that is a superior lubricating oil, depending upon the characteristics of the raw stock. The amount of propane used amounts to three to ten times as much as the

charge stock. By a series of settings at increasing temperatures it is possible to precipitate asphalt followed by lighter and lighter petroleum residues.

### **DUO-SOL PROCESS**

in this process, two solvents are used in a counter current system of flow and the feed is introduced at an intermediate point in flow system. It is a double solvent process that must be used extensively. One solvent dissolves paraffinic Hydrocarbon and the other dissolves naphthelnic hydrocarbons. A true counter current stripping operations is maintained as in one end of the extraction system; the outgoing cresylic acid solution is stripped of paraffinic material by pure propane and in the other end the outgoing propane solution is stripped of naphthenic material by pure cresylic. The heavy cresylic acid solution is pumped from one compartment to the next. It contains nine settlers or compartments. The heavy cresylic acid solution is pumped from one compartment to the next and the propane solution is also pumped but, in a counter, current manner. The feed is introduced in compartment 3 nearest the end at which propane is introduced.

### **CARBON REJECTION PROCESS**

This process takes place at an elevated temperature and pressure. It involves the breaking down of heavier and longer hydrocarbon chains into lighter ones. Lighter and shorter hydrocarbon chains are more useful. This thermal processing includes residue hydrocracking (RHP), advanced cracking, fluid coking, flexi- coping, vis breaking, delayed coking.

### **RESIDUE HYDROCRACKING PROCESS (RHP)**

This can crack atmospheric residue to produce middle distillates in a fixed-bed reactor with a novel hydro cracking catalyst durable to catalyst poisons such as asphaltenes. Hydro cracking processes using distillates as feedstock are commercialized worldwide. However, on account of catalyst deactivation, it is extremely difficult to directly hydrocrack hydrocarbon oil containing many metals and asphaltenes like atmospheric residue. The application of residue hydro cracking is being developed not such that it can be used in hydro desulphurization process and is also able to hydrocrack atmospheric residues from Middle East crudes without pre-treatment.

### **ADVANCED CRACKING REACTION PROCESS (ACR)**

ACR process Is a flame cracking method. It recovers head from the reaction gases of any feedstock including vacuum gas oil. It also produces high pressure steam (about 100kg km<sup>2</sup>), pitch which is useful for manufacturing electrodes and premium coke can be processed from the withdrawn quench oil. A specially developed acid gas removal system effectively removes carbon dioxide and the bulk of sulphur and polymer from the furnace gas prior to gas separation.

The ACR process permits the use of a wider variety of liquid feed stocks ranging from naphtha to vacuum gas oil or any blend of their distillates and including selected crude oils.

### **FLUID COKING PROCESS**

There is no upper limit on Conradson carbon residue suitable feedstock include vacuum residuum of all types, catalytic cracking, polymer vis breaker tar, shale oil, sands, bitumen, asphalt, whole and reduced tar. The fluid coking is a versatile process that is applicable to a wide range of heavy feedstocks and a variety of products. Fluid coking is a continuous fluid bed thermal cracking process for upgrading residual petroleum stocks to gas oil, naphtha, gas and coke. The feedstock should have a Conradson carbon residue of more than 5%. The liquid products from the Coker can provide large quantities of IOW sulphur fuel after being hydro treated with commercially available process.

### **VISBREAKING**

Even though this process has been applied to everyday oil refining. It has undergone several improvements with respect to Its process layout, safety operational standards and accordingly the present Visbreaking process differs accordingly, the present Visbreaking process differs considerably from old one \*. The Visbreaking process is a comparatively mild thermal cracking process mainly used to lower the viscosity and pour point of residue oil. The method has come back worldwide a convenient and cheap tool to upgrade heavy oils.

Cracking severity of the process is mud producing a relatively small number of lighter distillates, but the process still has an important role in reducing the amount of cutter stocks for example, straight run gas oil.

In principle the technology of Visbreaking process is very simple and the cracking reactions proceed without catalyst under comparatively low pressure.

### **FLEXICOKING PROCESS**

In this process, feedstocks should have more than 5% Conradson carbon residue and the same as fluid Coker. The flexicoking typically converts 98% of a vacuum residuum to gaseous and liquid products. More than 99% of the metals in the feed are concentrated in 2% solids purged from the system. About 95% of the total sulphur in the residuum can be recovered from the fuel products as elemental Sulphur via commercially available processes. This process converts about 95% of the gross coke to gas with a heating value of 889 to 1,068kcal/m<sup>3</sup> that can be burnt in process furnaces and boilers. The coke fines from a flexicoker contain most of the metals in the feedstock and may be suitable for metals in the feedstock and may be suitable for metals recovery. The flexicoking is an advanced process of fluid Coker integrating a coke gasifier with the fluid coking to decrease coke.

25% of the gross coke can be gasified in the steam gasifier to produce synthesis gas containing about 50mole %hydrogen and about 25 mol % carbon monoxide. This synthesis gas can be processed through shift reactions and CO<sub>2</sub> removal process. The heat required in the team gasifier is supplied by coke circulated from the air gasifier via the heater in the same way as conventional flexicoker. Dual gasification flexicoking process is developed to deal with the low colony gas produced from the flexicoker. By separating the steam gasifier from the air gasifier, dual gasification flexicoker can produce hydrogen rich synthesis gas.

### **DELAYED COKING**

The process produces coke, gas oil, and naphtha through the thermal cracking of heavy residue such as vacuum residue and thermally cracked. The feature of delayed coking process is that though there is enough residence time in reaction zone or coke drum, the thermal cracking and successive coking of heavy residue proceeds more sufficiently compared with other thermal cracking processes.

The coking process has the advantages of being capable of cracking heavy oils that are not easily processed otherwise, and yielding cracked gas oil, which is suitable as a feedstock for catalytic cracking process. The by-product coke can be used after calcining as material for electrode of aluminum smelting or electric furnace steel making if the impurity level of the coke is sufficiently low. It may be sold to the power generating station and burned as fuel. It can be used effectively if

activated in adsorption process as it has become activated carbon. Some impurities often associate the coke example: sulphur, metals like nickel and vanadium.

## **DELAYED COKING**

Delayed Coking is an endothermic reaction with the furnace supplying the necessary heat to complete the coking reaction in the coke drum. The exact mechanism of delayed coking that it is not possible to determine all the various chemical reactions that occur, but three distinct steps take place;

Partial vaporization and mild cracking of the feed as it passes through the furnace.

- Cradling of the vapor as it passes through the coke drum.
- Successive cracking and polymerization of the heavy liquid trapped in the drum until it is converted to vapor and coke.

## **USES**

### **LIQUID-PHASE APPLICATION**

In this phase application, activated carbon is used in powdered form. It is used: For removal from evolution of color, odor, taste or other objectionable impurities such as foaming or retarding crystallization.

- i. For concentration or recovery from solution of a solute. Usually, liquid treatment with powder is a batch process.

Activated is widely used to remove color from sugar, red palm oil. It removes protein and hydroxy methyl furfural from the glucose syrup rendering it colorless and stable. Treatment of water, it is also a broad - spectrum agent that effectively removes toxic or bio refractive substances. In dry cleaning industry, it is used for reclaiming liquid solvent that has become contaminated with dyes and rancid extracted oils and grease. Pharmaceutical uses include removal of pyrogens from solutions for injections, vitamin decolorizing and deodorizing and insulin purification'.

### **ii. GAS - PHASE APPLICATION**

It is used in gasoline vapor emission control canisters on automobiles. The working capacity of a for gasoline vapor is determined by the adsorption - desorption temperature differential, the rate at which purge air flow through the carbon canister and by extent to which irreversibly adsorbed high molecular weight gasoline components accumulate on the carbon. It is used in purification and separation of gases. Gas masks containing activated carbon are used to protect individuals from breathing toxic gases or vapor. It is used in nuclear reactor systems to adsorb radioactive gases in



carrier or coolant gases and ae radioactive gases for adsorbing and retaining radioactive materials long enough for isotopes to decay to safe levels of radioactivity before being discharged into the atmosphere. Activated carbon is used as the catalyst in the manufacture of phosgene from carbon monoxide and chlorine.

### iii. PRINTING INK

The four important properties of printing ink are drying time, printability, color and use properties. Printability is a function of the rheology of printing inks. The Rheology of printing inks is of the greatest importance. In a Newtonian liquid, stress

produces a flow. Generally printing inks are non - Newtonian. The most common terms used to describe Rheology are viscosity (resistance to flow); yield value (point at which a liquid starts to flow under stress. Thixotropy (decreasing viscosity with increasing agitation and dilatancy (opposite of thixotropy)

Drying is any process that results in the transformation of a fluid - printing ink film into a rigid form. Ink is said to dry when a print does not stick or transfer to another surface placed in contact with it. Physical or chemical mechanism, absorption, evaporation, precipitation, oxidation, polymerization, cold setting, gelation, and radiation curing accomplish it.

### TYPES OF PRINTING INK

Generally, there are four main classes of printing ink based on variation in physical appearance, composition, method of application and drying mechanism.

**1. LITHOGRAPHIC INKS:** These are formulated to run in the presence of water. since water is used to create the non-image area of plate. The ink film is thinner than letterpress therefore pigment content must be higher. Most lithographic printing is done with an offset blanket. When the ink is transferred from plate to rubber blanket, which In turn transfer the Image to the surface being printed. It is termed "offset' It Is done with offset blanket.

**2. LETTER PRESS:** These inks are viscous, tacky, the vehicles are oil or ink has mineral oil as vehicle and drying is accomplished by adsorption. When the letter is pressed, image is transferred to a rigid surface such as plastic or two - piece metal container. The ima9e is transferred to a blanket and then to the printed surface.

**3. ROTOGRAVURE:** these are low viscosity (liquid) inks that day by solvent evaporation. They are formulated with a wide range of resin vehicles. There are four types based on certain specific applications, which designate the type of binder and solvent used. TYPE A is used for

publication printing and is the cheapest. TYPE B is used for publication printing on better grade stocks than TYPE A. TYPE C is used for various types of packaging. TYPE D is used for package printing, primarily food cartons.

**4. FLEXOGRAPHIC:** These are low viscosity inks which dry by solvent evaporation. absorption in the surface and decomposition they are chemically different from others. Two main types of flexographic ink are water and solvent. Water inks are used on adsorbent paper stocks such as craft or light weight paper. Solvent types are used on films such as cellophane, polyethylene or polypropylene. They may also be used on some paper surfaces.

There are several specialized inks, which may be used in different printing P<sup>^</sup> ^88- They are metallic ink, watercolor ink, cold - set ink and magnetic ink. Others are web oP8et Inka, sheet offset Inks and metal decolorizing Inks.

## CONCLUSION

Based on the fact and Information presented in the above discussions, I hereby make the following conclusions.

From the experimental results, it could be inferred that useful resources could be recovered from crude oil sludge by solvent de-asphalting, delayed coking, activation and using asphaltic sludge as pigment in print ink formulation respectively.

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