**EXTRACTION AND APPLICATION OF LIGNIN AS A SURFACTANT BASE IN HEAVY OIL MANAGEMENT**

**BY**

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**BEING A PROJECT PROPOSAL SUBMITTED**

**TO**

**THE DEPARTMENT OF CHEMICAL ENGINEERING FACULTY OF ENGINEERING AND TECHNOLOGY LADOKE AKINTOLA UNIVERSITY OF TECHNOLOGY, OGBOMOSO, OYO STATE, NIGERIA**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF TECHNOLOGY (B.TECH) DEGREE IN CHEMICAL ENGINEERING**

**APRIL, 2020**

# **INTRODUCTION**

## **1.1 Background of Study**

Viscosity reduction in Heavy Oil in a bid to aid its transportation through pipelines has been over the years achieved through various means, one of which is emulsification. Emulsification involves the dispersion of one medium as droplets in another - both medium ordinarily immiscible - thereby reducing the interfacial tension, usually in the presence of surfactants, a water/oil emulsion, with significantly reduced viscosity is achieved. Emulsions of crude oil and water occurs at many stages which includes drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities and refineries. A water in oil emulsion is most often created when mixing water and crude oil because the surface active amphiphilic molecules in the crude are mostly oil soluble due to their low polarity (depending on pH for fatty acids) and molecular weight [1].

Crude oils, especially the heavy oils, contain large quantities of asphaltene, a high molecular weight polar component, that act as natural emulsifiers. Other crude oil components are also surface active: resins, fatty acids such as naphthenic acids, porphyrins, wax crystals, etc, but most of the time they cannot alone produce stable emulsions [2]. There are large varieties of emulsification methods such as simple shaking, mixing with rotor-stator systems, liquid injection through porous membranes, or high pressure devices (homogenizers, liquid jets), etc. [3]. In some cases, multiple emulsions such as water in oil in water (W/O/W) or oil in water in oil (O/W/O) can be found. Oil-water emulsions are fine dispersions of oil in water (O/W) or of water in oil (W/O), with drop sizes usually in the micron range (1, 2). In general, emulsions are stabilized by surfactants.

In oil exploration, exploitation and processing, surfactants are involved in every step [4]. Surfactants are surface active substances, which in solution, (especially aqueous) tend to congregate at the bounding surfaces – air-solution surface, of the container and the liquid-liquid interface, thereby reducing the surface tension (or interfacial tension) between the interfaces. Surfactant molecules are known to consist of two distinct parts – the hydrophilic and the hydrophobic parts, oleophobic and oleophilic part in oil soluble surfactants. Based on the charge on their hydrophilic base, surfactants are categorised as anionic, cationic, and amphoteric. Although all surfactants contain hydrophilic and hydrophobic chemical groups, the relative dominance of each group differs. The hydrophilic–lipophilic balance (HLB) of surfactants is determined by the chemical nature of the hydrophilic and hydrophobic moieties within the surfactant molecule.

Generally, the hydrophobic part of the surfactant interacts with non-aqueous phase and hydrophilic part of the surfactants interacts with aqueous phase. Most surfactants currently used in industries derive their bases from petroleum products. In addition to their various roles in oil and gas production, surfactants are used in the formulation of petroleum products, and also in oil pollution removal for Environment protection.

In heavy oil and other related operations, the main parts played by surfactants are summarized as [5]:

* Dispersing agents and additives for drilling muds,
* Surface tension reducers in Enhanced Oil Recovery,
* Demulsifiers for crude oil and emulsifiers for hydrocarbon transportation,
* Scale-removing agents and corrosion inhibitors.

Rising environmental concerns and depletion of petrochemical resources has sparked interest in the use of biorenewable and more environmentally friendly materials as surfactant base. One of such biorenewable and naturally occurring material is Lignin.

Lignin, a class of complex organic polymers that form key structural materials in support tissues of vascular plants [6], is the most abundant noncarbohydrate biological material [7], second in abundance only to cellulose in the class of naturally occurring polymers [8], and one of the three main materials found in the cell walls of lignocellulosic materials. It is a major by-product of industrial processes involving the retrieving and use of other plant components such as polysaccharides for use as feedstock for further processes e.g. paper making, hence, it is widely available in most cases, as waste product from such processes. Such industrial processes has been said to produce about 150 million tonnes of lignin annually, much of which is being burnt for power.

Lignin being an aromatic macromolecule and its relative abundance makes it a viable option in use as feedstock for value added materials (in this case – surfactants) in place of petroleum based options. Lignin is primarily extracted from pulping spent liquors, which also contain other organic impurities, e.g., hemicellulose; and inorganic impurities originating from pulping chemicals. Lignin has great potentials for use as a surfactant given its hydrophobic aromatic configuration [9].

## **1.2 Problem Statement**

The quest for a sustainable and biorenewable feedstock for use as surfactant base drives the research into Lignin as a viable option for a surfactant base for use in manufacture of surfactants to be used in heavy oil management.

## **1.3 Objectives**

* To extract Lignin from biomass (Saw dust and maize stalk)
* To modify the extracted Lignin for use as surfactant base
* To study the viability of surfactant thus produces, through the analysis of its emulsion

## **1.4 Significance of Study**

Surface active agents (surfactants) are chemicals that can accumulate at the surface of a liquid, or interface between two phases with the role of changing the surface tension of the interface. They are very essential in heavy oil production. Therefore, this project will assist in the extraction techniques and contribute to the literature on Heavy Oil surfactants.

## **1.5 Scope of Study**

This project work will be based on the use of Milled wood (saw dust), Maize stalk and water which will be gotten locally at Ogbomoso, Oyo State. This project work will also be limited to the use of NaOH and H2SO4 for extraction of Lignin.

**LITERATURE REVIEW**

**2.1 Bitumen**

Bitumen is a black, sticky, and highly viscous liquid or semi-solid form of petroleum found in natural deposits or produced by removing the lighter fractions (such as liquid Petroleum gas, petrol and diesel) from crude oil during the refining process. Bitumen is traditionally regarded as a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles are considered to be asphaltenes together with an absorbed sheath of aromatic resins that act as a stabilising solvating layer. Away from the centre of the micelle, there is a gradual transition to less polar aromatic resins, these layers extending outwards to the less aromatic oily dispersion medium.

Good crude oils and proper distillation processes can enhance bitumen properties. Generally, heavier crude oil gives higher bitumen yields [10]. From a commercial point of view bitumen is a low-cost thermoplastic material that has been widely used in roofing and pavement application, paving mixtures, and industrial products for a long time. In both paving and industrial applications, the bitumen should be resistant to climate and more demanding traffic loads, for which reason rheological properties play a key role in different aspects [4–6]. From a functional point of view, the bitumen has to be fluid enough at high temperature (≈160 °C) to be pump-able and workable to allow for a homogeneous coating of aggregate upon mixing.

With its first discovery in the year 1900, Nigeria has the second largest deposit of bitumen with an estimated reserve of 16 Billion Barrels (mineandsteel.gov.ng). With majority of Bitumen used in the construction industry, as constituent product for paving and roofing, its thermoplastic and waterproofing behaviour makes it ideal for a variety of applications. For of ease of transportation and application, it is essential that Bitumen behave as a mobile liquid. This can be achieved through heating, dissolving or emulsifying. However, the major means of viscosity reduction in Bitumen, as it’s relatively solid at ambient temperature involves heating to a temperature range of 140 -230oC, depending on the Bitumen grade (Shell Bitumen Handbook, 6th Edition).

**2.2 Emulsion**

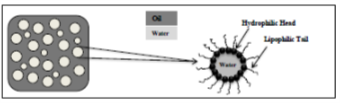
An emulsion is a colloidal mixture of two or more immiscible liquids with one liquid having a dispersion of another liquid in it. It consists of droplets of one liquid in another liquid medium, sometimes achieved through the use of surfactants. Interphacial tension, the property upon which the miscibility of two liquid phases depend is the Gibb’s free energy per unit area of interphase at fixed temperature and pressure, and is due to variance in molecular interaction for a molecule near the surface and an equivalent molecule within the bulk fluid (SLB Oilfield Glossary). For miscibility to be realised, a reduced interphacial tension between the fluid surfaces is to be achieved. Depending on the phase in abundance (continous phase) and that dispersed in the other (dispersed phase), two types of emulsions exist – water-in-oil (w/o) emulsion and oil-in-water (o/w) emulsion.

An emulsion is not contained only water and oil; it may also contain some solid particles and even gas. Inherently, an emulsion is an unstable system due to the unfavourable contact between oil and water phases. Although, some emulsions are stable as a result of the small drop sizes and the existence of interfacial film, which surrounds the drops [11,12,13]. The emulsions formed without adding any surface active material would not be stable, and the emulsion phases will start to separate in different layers based on their density differences while the addition of surfactants produces stable emulsions for a longer period of time.

**2.2.1 Types of Emulsions**

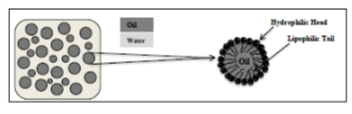
There are generally three types of emulsions know as water-in-oil (W/O), oil-in-water (O/W) and water-in-oil-in-water (W/O/W) which is also known as multiple emulsion [14]. If the oil is dispersed phase, the emulsion is named O/W, but if the aqueous medium is the dispersed phase, the emulsion is named W/O. The different types of emulsions are summarized below.

* **Water-in-Oil Emulsions:** This is an emulsion where the continuous phase is usually made up of hydrophobic materials such as oil and the dispersed phase is water [15]. These emulsions contain a mixture of a solvent, a surfactant and water. Several studies has shown that stability is the most important characteristics in W/O emulsion.



**Fig 2.1:** W/O emulsion and emulsifiers on the surface of the dispersed phase (Water).

* **Oil-in-Water Emulsions:** In this type of emulsion, the oil exists at the dispersed phase. This type of emulsion can result into a financial loss in production factories if not treated properly [16].



**Fig 2.2:** O/W emulsion and structure of emulsifiers on the surface of the dispersed phase (Oil).

**2.3 Surfactant**

For a system of naturally immiscible phases to mix and thus form an emulsion, reducing the interphasal tension between the constituent phases becomes important. Surfactants work by adsorption at the oil-water interphase, preventing drop growth and separation into the original oil and water phases. According to Langevin *et al*, 2004, after adsorption, the surfaces become viscoelastic and the surface layers provide stability to the emulsion. Spontaneous adsorption occurs at the surface when surfactant is added to oil or water, thereby the decreasing the surface tension.

As most surfactants similarly consists of a hydrocarbon tail (branched, linear and aromatic) and a polar/non-polar head, they are classified according to the charge on their polar head group. An anionic surfactant is one whose polar head group carries a negative charge, while a surfactant is classified as cationic if its polar head group carries a positive charge. Should the surfactant head consist of oppositely charged groups, it’s termed zwitterionic. These three classes belongs to the Ionic surfactant class, while the second class – Non-ionic surfactants has no charged groups on their head.

In most of these surfactants, the polar group is produced by the polycondensation of ethylene oxide that results in a polyether chain. The most common surfactants are the ethoxylated alcohols, alkylphenols, acids, and esters. Non-ionic surfactants are much less sensitive to electrolytes than anionic surfactants. They tend to locate preferentially at the interface between a polar and a non-polar phase. Surfactants are also capable of self-association in aqueous or non-aqueous solutions. When the surfactant concentration increases in the aqueous phase, the surfactant molecules saturate the interface before accumulating in the solution. At some point, the surfactant molecules start aggregating into the so-called micelles, a self-association structure in which the hydrophobic tail is removed from the aqueous environment.

Lignin as a naturally occurring polymer has been considered as surfactant base, given its abundance, little value-added utilization and its basic composition of three aromatic groups.

**2.4 Lignin**

Boerjan et al in 2003 described Lignin as the second most abundant naturally occurring polymer (the most abundant being cellulose), accounting for 30% of the organic carbon in the biosphere and is a structural material in plant cell walls. It fills the spaces between cellulose, hemicellulose and pectin components in the cell walls, strengthening cell walls and thus, the plant as a whole. It is a highly branched and amorphous bio-macromolecule whose composition depends on the plant source, and sometimes the extraction method employed, as chemicals used results in chemical modification of the three-dimensional network through the cleavage of bonds between different lignin monomers, or the covalent attachments to polysaccharides, creating differently sized lignin fragments.

Lignin is unique as a plant cell wall biopolymer due to its heterogeneity, lack of defined primary structure and aromatic functionality. It can however be rationalized as the polymerized product of the three basic phenylpropane monomers as repeating units known collectively as “monolignols”: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. At least 70 tons of Lignin is produced annually, the bulk of it from kraft and sulfite pulping processes in the pulp and paper industries, where Lignin is separated from lignocellulosic material (wood) to produce black liquor. However, only less than 2% of the lignin produced from pulping industries was value-addedly utilized, while the rest is sometimes burned as a low-value fuel for energy supplement or left to waste, leading to environmental pollution and underutilization of a potentially valuable material for value-added applications.

However, Lignin has over the years been applied as a phenol substitute in phenol formaldehyde resins, as a substituent in Lignin-epoxy resins used in printed circuit boards, adhesives used in Fibreboards, binders in mortar and construction systems, metal sequestration in solutions and in vivo, biodegradable plastic additive, basis of gel formation, polyurethane copolymers, etc. The alkaline method of extraction as employed by Ibrahim and Azian(2005), Ibrahim, Nadiah & Azian (2006), Ibrahim, Yusuf and Hashim(2007), Alriols et al (2008), Harsano et all(2016), Tan et all(2019), Pan et al(2006), Fu et all(2010), Sun et all(2005) and Setiati et al (2019), is employed in this research.

The Lignin polymer chain is hydrophobic in nature, while consisting of hydrophilic hydroxyl and carboxyl groups. Given the hydrophobic nature, modifying the extracted Lignin to increase its hydrophilicity, by adding a hydrophilic sulphonate group to the aromatic chain through sulphonation, thereby producing Lignosulphonate (Alwadani, 2018).

**2.5 Lignosulfonate**

Lignosulphonates are water-soluble poly-electrolyte polymer which are anionic in nature. With hydroxyl groups replaced by sulphonate groups, the hydrophilicity of Lignin is improved, making for a hydrophilic-lipophlic balance (HLB) of 11.6. On an industrial scale, Lignosulphonates are mostly obtained from spent pulping liquor from pulping industries. However, Lignosulphonates obtained from this source may be contaminated with polysaccharides and inorganic pulping chemicals, which makes its direct use challenging.

Lignosulfonates have been used across a variety of applications such dye dispersants, chelating agents and water reducers for cement [17]. Lignosulfonate is an anionic surface-active polymer capable of exerting electrostatic repulsion and steric hindrance and it is often applied as a water reducer for concrete admixtures. Lignosulfonates are gotten from lignin by sulfomethylation and this product it also can be used as concrete admixtures. For example, Ouyang et al. [18] used a sulfomethylation technology on alkali lignin and revealed that the resulting lignosulfonate functioned as a concrete dispersant. Although sulfonation is a viable chemical pathway for preparing lignosulfonates from various industrial lignins, this chemical modification requires acidic conditions. As a negative, acidic conditions can also render undesirable inter-lignin condensation reactions, lowering the application viability of the sulfonated lignin product.

**MATERIALS AND METHODOLOGY**

**3.1 Introduction**

This chapter discusses the methodology applied in the extraction of Lignin from wood and maize stalk, modification (sulphonation) into Lignosulphonate and its application in viscosity reduction in Bitumen. It explains the experimental process involced in the extraction and modification, and methods used in obtaining properties of materials at each stage of the process.

**3.2 Materials**

Materials used includes Milled wood (saw dust), maize stalk, NaOH, H2SO4, Sodium Bisulphite, Distilled Water. Equipment/apparatus used includes Filter paper, funnel, conical flasks, measuring cylinders, oven, and homogenizer.

**3.2.1 Biomass (Milled Wood and Maize Stalk)**

According to [reference], milled wood contains about [lignin comp.] of lignin with other materials like cellulose and [whatever that is] making up the remaining mass of the wood material. Milled wood is chosen for its relative local availability and its high surface area due to its reduced particle size, thereby relieving the study of the particle size reduction process. The milled wood is obtained from local saw mills.

Maize Stalk on the other hand is a waste material left after corn harvest. In its wake, it is sometimes used as feed for cattles, sheeps and other ruminants. When dried (low moisture content), it becomes less viable as feed material, and thus a waste.

**3.2.2 Material Preparation**

The milled wood is sun dried till relative dryness is achieved, then sieved in a sieve shaker with the maximum mesh size used being [max mesh size used]. For the maize stalk, it is sun dried its size is reduced through cutting and further in a mortar and pestle, then sieved in a sieve shaker of the same specification as above.

**3.3 Lignin Extraction**

In this study, the alkali extraction process is employed for the extraction of lignin from wood. This involves refluxing milled wood in [prop] proportion with 2% NaOH solution, at 100oC for 5 hours. The reflux mixture obtained is filtered, the filtrate is diluted with equal volume of distilled water, after which 98% H2SO4 solution is added to attain a pH of 2. The mixture is left for 8 hours, after which Lignin would have been fully precipitated. The mixture is filtered and the residue obtained is dried in an oven at 70oC for [time] (Setiati et al 2017).

**3.4 Sulphonation**

The sulphonation process involves the addition of a sulphonate group to the Lignin molecule. The purpose of this is to improve the surfactant’s hydrophilicity, by substituting hydroxyl groups with sulphonate groups, \*\*tipping its Hydrophilic-Lipophilic balance (HLB) above 10\*\*. 5 g of Lignin obtained from above was added to 250ml 0.3M solution of NaHSO4, stirred and heated to 97oC for 4 hours. The solution was filtered to achieve unreacted lignin (solid). The filtrate is lignin and NAHSO4. The filtrate was distilled at 100oC till water was removed from the filtrate (dryness is attained). 200ml of methanol solution was added to the dried filtrate and stirred for 30 minutes. Filtrate is dissolved lignin in methanol while residue is the NAHSO4. The filtrate was distilled at 70oC (Ariestiana et al 2019).

**3.5 Surfactant Analysis**

The dried Lignin obtained from the extraction and the Lignosulphonate after modification is analysed using Fourier Transform Infra Red (FTIR).

## **REFERENCES**

[1] - Acevedo, S., Escobar, G., Gutierrez, L.B., Rivas, H. and Gutierrez, X. (1993) Interfacial Rheological Studies of Extra- Heavy Crude Oils and Asphaltenes - Role of the Dispersion Effect of Resins in the Adsorption of Asphaltenes at the Interface of Water-In-Crude Oil-Emulsions. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, **71**, 65-71.

[2] - Lee, R.F. (1999) Agents which Promote and Stabilize Water-in-Oil Emulsions. *Spill Science and Technology Bulletin*, 5, 117-126.

[3] - Walstra, P. (1993) Principles of Emulsion Formation. *Chemical Engineering Science*, **48**, 333-349.

[4] - Bhardwaj A. and Hartland S. (1993) Applications of surfactants in petroleum industry, *J. Disp. Sci. Technol.*, **14**(1), 87-116

[5] – Bognolo G. (2000) Surfactant applications in the context of structure-performance relationships, in Annual Surfactants Review, *CRC Press, Boca Raton (Fla.)*, **3**, 1-65.

[6] - https://en.wikipedia.org/wiki/Lignin

[7] - Holtzapple, M. T. (2003). LIGNIN. Encyclopedia of Food Sciences and Nutrition, 3535–3542. doi:10.1016/b0-12-227055-x/00699-4

[8] - Thakur, V. K., Thakur, M. K., Raghavan, P., & Kessler, M. R. (2014). Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review. ACS Sustainable Chemistry & Engineering, 2(5), 1072–1092. doi:10.1021/sc500087z

[9] - Y. Jiao, Z. Xu, W. Qiao, Z. Li, (2007) Research interfacial properties of the novel

lignosulfonates*, Energy Sources Part A* 29 (15) 1425–1432, https://doi.

org/10.1080/00908310600710699.

[10] - Read, J.; Witheoak, D. (2003) The Shell Bitumen Handbook, 5th ed.; *Thomas Telford Publishing: London, UK*

[11] - E. Chrisman, V. Lima, P. Menechini, (2012) Crude Oil Emulsion- Composition Stability and Characterization, in *M.E.-S. Abdel-Raouf (Ed.), InTech, 3rd ed.*, InTech, Janeza Trdine 9, 51000 Rijeka, Croatia, Egypt,: pp. 1–240.

[12] - R. Pal (2002), Novel shear modulus equations for concentrated emulsions of two immiscible elastic liquids with interfacial tension, 105 21–33.

[13] - H. Zhu, Z. Guo (2016), Understanding the Separations of Oil / Water Mixtures from Immiscible to Emulsions on Super-wet-able Surfaces, J. Bionic Eng. 13 1–29. doi:10.1016/S1672-6529(14)60156-6.

[14] - V. Hoshyargar, A. Marjani, F. Fadaei, S. Shirazian (2012) Prediction of flow behavior of crude oil-in-water emulsion through the pipe by using rheological properties, *Orient. J. Chem.* 28 109–113. doi:10.13005/ojc/280116.

[15] - J.T. Foley, P. Forest, R.H. Rogers (1966) *United States Patent*

[16] - M.E.-S. Abdel-Raouf (2012), Factors affecting the stability of crude oil emulsions, in: *Manar El-Sayed Abdul-Raouf (Ed.), Crude Oil Emuls. Stab. Charact* pp. 183–204.

[17] - Zhou, X.; Zhou, X.; Tang, X.; Xu, Y. (2018)Process for calcium xylonate production as a concrete admixture derived from in-situ fermentation of wheat straw pre-hydrolysate. *Bioresour. Technol.*, 261, 288-293

[18] - Ouyang, X.; Ke, L.; Qiu, X.; Guo, Y.; Pang, Y. (2009) Sulfonation of alkali lignin and its potential use in dispersant for cement*. J. Disper. Sci. Technol.,* 30, 1–6.