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Performance Evaluation of Acid-Precipitated Kraft Lignin as A Renewable Feedstock for Biomass Briquettes

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Abstract
Academic and industrial sectors have considered several possibilities in their pursuit of building a resource-based society. In its efforts to accomplish these ends, the forest industry may take the lead in recycling process byproducts into new products like pulp and lumber. Producing energy is one of the most fundamental needs of modern civilisation. Bioenergy may be produced from byproducts of wood processing and cellulose mills. Adding industrial forest leftovers like lignin to densified biomass raises storage, transportation, and handling concerns; additionally, the resulting energy product may have better characteristics, adding value to the chain. The current research looks at how various acid precipitation techniques affect kraft black liquor lignin recovery and assesses the fuel properties of the separated lignin for briquette making. Lignin treated with acetic acid, on the other hand, had the lowest nitrogen and sulphur levels, suggesting that burning releases less nitrogen oxides and sulphur oxides.
Keywords: *Kraft black liquor, Lignin, Acid, Proximate, Ultimate*

I. INTRODUCTION

Recent years have seen a surge in interest in lignocellulosic biomass as a possible bioenergy source due to factors such as its low cost, availability, and renewability. Brazil is the world's largest exporter and producer of coffee, so naturally there is an abundance of discarded coffee grounds, also known as husks, which may be recycled into bioenergy at little cost and with little environmental impact. The biggest problem with using bulk biomass to make energy is how cumbersome it is to move, store, and work with due to its non-standard form and very low bulk density. Due to its low energy density and high humidity, the biomass drying stage consumes a significant amount of the energy supplied throughout the thermochemical process, hence reducing energy efficiency.

The mechanical process of biomass compaction is one approach to reuse these resources. Solid biofuels briquettes are created by compressing raw materials. Because of their homogeneity, consistent size and shape, and higher density compared to bulk biomass, these materials are more convenient to work with and transport, and they also have a higher energy density and longer storage capacity. Briquettes are a cleaner-burning alternative to firewood due to their size, exact form, and regular humidity. Therefore, briquettes made from garbage can be an effective and environmentally responsible substitute for firewood or fossil fuels. One way to enhance the quality of briquettes is to use additives. The correct additives, when added to briquettes, can greatly improve their physical, thermal, and mechanical properties. Kraft lignin is a waste product of the pulp industry. It is burned in the recovery boiler to produce steam and thermal energy, which are vital for many industrial operations. Unfortunately, kraft lignin, a valuable aromatic source, has no viable recycling options. It has the potential to be turned into a wide range of valuable goods due to its accessibility, low cost, complexity, and plenty of functional groups.

Lignin has great potential as a component of biorefinery chemicals, polymeric materials, phenolic foams, and biofuels, according to a number of studies.

Thermoplastic lignin has the potential to be a binder additive in briquette production. Unfortunately, studies examining the efficacy of kraft lignin in this context are few. In addition to being a sustainable and ecologically sound way to make briquettes, lignin possesses adhesive properties, a high calorific value, and the potential to improve mechanical and energy characteristics, making it an intriguing green binder. Due to its higher carbon and hydrogen content and lower oxygen content, lignin has a higher calorific value (25.54 MJ/kg) than polysaccharides.

II. REVIEW OF LITERATURE

Ulakpa, Wisdom Chukwuemeke et al., (2023) As a result of the many negative outcomes associated with using non-sustainable power sources, renewable energy is gaining increasing attention. Among other things, it has been shown that biomass from horticulture harvests may be used as a nonrenewable energy source, making it an attractive option for steam-added product separation or production. Most of the lignin that is burnt to recover energy nowadays comes from the pulp and paper industry, which generates 50 to 70 million tonnes per year. The potential use of lignin, a naturally occurring aromatic polymer rich in functional hydroxyl groups, in the creation of polymeric goods has piqued the curiosity of both academics and commerce. When it comes to polymers made from lignin, polyurethanes (PUs) rank high on the list of importance due to their wide range of applications. Sticky materials, glue, biomaterials, cement, furniture, and architectural constructions are just a few of lignin's many applications. The continuous investigation for new and late green/supportable uses for rice husk and trash includes a variety of specialised, modern, and other eco-friendly power applications. Additionally, the basic information on agricultural waste uses is provided, and the amount of silica that can be extracted from rice husk is compared to other agricultural waste sources.

Waghmode, Meghmala et al., (2023) It is critical to use waste as a fuel source immediately due to the high cost of gasoline. The biomass of dead flowers and leaves found in the environment may be used as raw materials to make bio-briquettes. The study utilised a variety of leaf litter wastes, including those from almond trees, ashoka trees, cluster fig trees, marigolds, tuberoses, and roses. In order to speed up the degradation process, the waste was treated with microorganisms such as Lactobacillus plantarum ATCC 8014 and Lactobacillus brevis ATCC 14869. Manual pressure, wet briquetting, and a cylindrical mould were utilised in the formulation of the briquettes. As a synthetic binder, paper pulp and wheat bran were mixed in a 35:5 ratio. Moisture, volatile matter, ash, fixed carbon, and other components are part of the first analysis. Density, calorific values, FESEM, FT-IR, and TGA were the last criteria for evaluating bio briquettes. Briquettes made from untreated lignocellulosic biomass and briquettes sold in stores were used for the comparisons. The specifications of briquettes produced from microbiologically treated waste are as follows: a density of 0.26 kg/cm3, a calorific value of 5968.20w kJ/Kg, a moisture content of 8.4%, a volatile matter content of 10%, an ash content of 13.65%, a fixed carbon content of 67.95%, a maximum burning time of 17 minutes, and a minimum ignition time of 3 minutes. Bales produced from raw waste have a density of 0.20 kg/cm3, a calorific value of 4205.10 kJ/Kg, a moisture content of 10.8%, a volatile matter content of 15%, an ash content of 15.11%, and a fixed carbon content of 59.05%. Bio briquettes treated with microbes provide new possibilities for fuel production and efficient management of agricultural waste, according to this comparative research.

Figueirêdo, Monique et al., (2022) Biofuels, biobased chemicals, and performance materials may all be sustainably made from lignocellulosic biomass. The time-tested method of rapid pyrolysis can efficiently transform biomass into pyrolysis liquids, which are also called bio-oils. As a result of its adaptability to different feedstocks, cheap cost, and high energy conversion efficiency, rapid pyrolysis technology is attracting a lot of attention as a potential technology for converting biomass. This has led to the launch of several new businesses all over the world. The complex and diverse organic composition of bio-oils makes upgrading them a laborious but necessary process. Separating pyrolysis liquids into an aqueous sugar-rich phase and a water-insoluble pyrolytic lignin (PL) fraction is possible via a simple water fractionation. Because of their distinct compositions and reactivity, the individual fractions can be converted using highly effective procedures that are made possible by this separation process. For instance, fermentation may make use of the fractions high in sugar, while depolymerization of the phenolic-rich PL can provide energy-dense streams and a variety of platform chemicals. Novel PL characterisation methods and valorisation strategies are being investigated to support its growing use. Next, the current status of PL processing utilising oxidative and reductive (catalytic) techniques, or a mix of the two, is reviewed, followed by a detailed discussion of the rapid pyrolysis process and PL characterisation attempts. There includes a discussion of potential uses and suggestions for further study.

Sujan, S M Asaduzzaman et al., (2020) The processes of pelletization and briquetting have been widely employed to increase the energy and mass density of biomass. Pellet production may make use of biorefinery waste lignin in addition to more traditional raw materials, meeting the rising demand for pellets. In order to make bioethanol, sugarcane bagasse (SB) is treated with sodium hydroxide (NaOH) at concentrations of 8% and 16%. The resulting lignin is then utilised to make pellets. Pellets with varying compositions of SB and Lignin1 were produced using varying applied pressures (5kN, 10kN, 15kN, and 20kN), as were SB, Lignin1 (8% NaOH treated SB), Lignin2 (16% NaOH treated SB), and so on. As the pelletization pressure was increased, the pellet density and heating value increased as well. Lignin1 has the greatest heating value of the samples at 20kN, which is 3581.54 kcal/kg. The maximum heating value (3456.21 kcal/kg) was seen in the pellet composition of 40% SB and 60% Lignin1, and the results demonstrated that 5kN is sufficient to create pellets from various SB and Lignin1 compositions.

Cesarino, Igor et al., (2012) With 30 percent of the biosphere's organic carbon coming from lignin, it is the second most prevalent biopolymer on Earth, after cellulose. Because it provided the first tracheophytes with a means of standing upright and because it waterproofed the vascular tissue, it allowed for the long-distance transport of water and solutes, making it an essential evolutionary adaptation of plants as they moved from an aquatic to a terrestrial habitat. Lignin is the main component of plant cell walls that makes biomass resistant to industrial processing, even though it is needed for plant growth and development. Lignin cannot be degraded by a single enzyme due to its non-linear aromatic polymer structure, which is composed of many monomer units joined by chemically varied and less reactive connections. Therefore, understanding what makes plant biomass resistant, particularly the complex phenolic polymer lignin, is crucial for developing biofuels and other bio-based products from lignocellulosic feedstock in a sustainable and environmentally friendly manner. We review what is known about plant lignin metabolism, how it affects biomass recalcitrance, and new approaches to manipulate biomass recalcitrance by metabolically engineering the lignin pathway. Also covered are developments in sugarcane research pertaining to lignin and the crop's prospective usage as a second-generation biofuel crop.

III. MATERIALS AND METHODS

For this investigation, the kraft black liquor was sourced from a variety of hardwood species utilised by the Indian kraft pulp and paper production company, including Acacia mangium, Acacia crassicarpa, and Eucalyptus spp. The kraft pulp's Kappa value decreased from 16 after heating to 10 after oxygen delignification. The products were procured from two Mumbai, India-based labs: HiMedia Laboratories Pvt. Ltd. and Merck India Pvt. Ltd. There was a 97% purity level for the analytical-grade sulfuric acid, a 99% purity level for the glacial acetic acid, and anhydrous citric acid. The deionized water used in all of the tests was supplied by the laboratory's purification equipment. All chemicals were used at the analytical reagent (AR) grade level without further purification.

Isolation of Lignin from Kraft Black Liquor

The kraft black liquor had its lignin removed by acid precipitation. The black liquor was first dissolved using demineralized (DM) water. The black liquor and water were kept at a weight ratio of 1:12. Slowly adding 6M sulfuric acid to the diluted black liquor solution maintained a pH level of 2. A same process was used to maintain the precipitation's pH between 3, 4, and 5. Phosphorus readings of 3, 4, and 5 were the end outcomes of a similar precipitation process with 99% acetic acid and 50% citric acid anhydrate. After filtering out the precipitate, the solution was washed with deionized (DI) water to bring the pH level back to neutral. Following drying, the lignin precipitates were repeatedly weighed until they reached a constant mass. The weight ratio of dried lignin to deionized water was 1:300 in a reflux flask. Filtering, drying, and periodically weighing the lignin until their masses stayed constant was the next stage.

Briquetting Process

The briquetting procedure was carried out using a hydraulic press and an apparatus that consisted of a bottom punch, a die, and an upper punch. A controlled environment was used for briquetting at the Bioenergy and Biomass Conversion Laboratory. The pressure was maintained at 500 bar since it was the minimal pressure required to create lignin briquettes of a specific briquette strength. Briquetting was done using a 3.5-ton hydraulic jack to create a 30-mm-diameter cylindrical briquette. In comparison to the conventional approach, which usually requires 100 bar of binder to produce a briquette, this one produced a higher briquetting pressure. Typically, 500-1000 bar is required for the Komarek method's binderless briquette manufacture. The resultant lignin briquettes are shown in Figure 1.

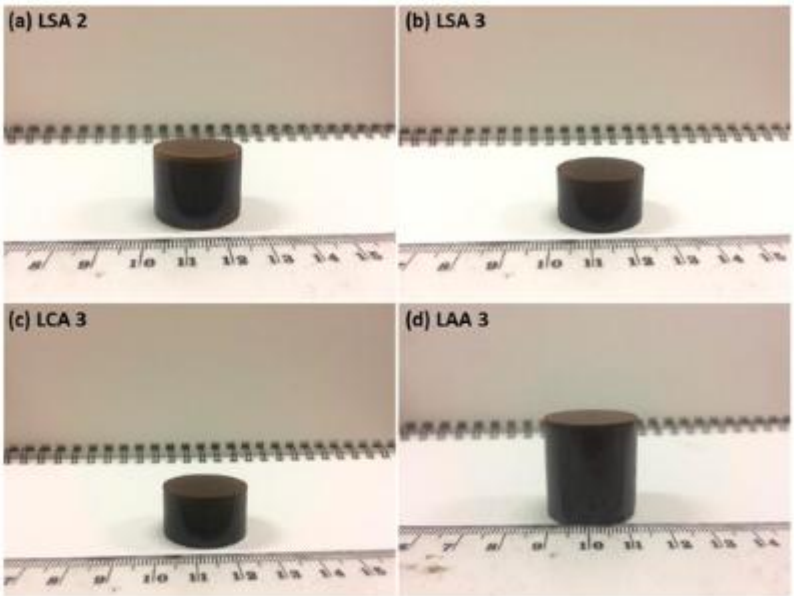

Figure 1: Lignin briquette

Determination of Lignin Purity

To test how pure the lignin extracted from black liquor was, the Klasson lignin method was used, as outlined in the TAPPI T-222 OM-02. One step of the test was to combine 1 gramme of lignin (a) with 15 millilitres of 72% sulfuric acid, and then to stir the mixture at 200 revolutions per minute using a magnetic stirrer for two hours. The sulfuric acid level was reduced to 3% after boiling the dissolved sample for 4 hours. Separation of the solution and precipitate was achieved by use of Whatman 42 filter paper. Once the residue had dried after being washed with DI water to neutralise its pH, it was weighed at regular intervals until it achieved a constant weight (b). Three rounds of testing were conducted on each version.

Proximate analysis

The moisture content, volatile matter, ash content, and fixed carbon of the generated lignin briquettes—properties of the fuel—were determined by proximate analysis. In accordance with the Bureau of Indian requirements' solid fuels requirements (BIS IS 1350, Part I), the study was carried out. The moisture content was determined by oven drying, the volatile matter by controlled heating, and the ash content by a muffle furnace, and the fixed carbon by taking the difference.

Ultimate Testing

The elemental composition of the purified lignin was determined by doing extensive tests on carbon, hydrogen, nitrogen, sulphur, and oxygen. The analysis was conducted using an elemental analyser from CHNS in compliance with ASTM D3176. The residual oxygen content was determined by removing the values of carbon, hydrogen, nitrogen, sulphur, and ash from the total content.

IV. RESULTS AND DISCUSSION

Effect of Acid Type on the Proximate Value of Isolated Lignin

Table 1 displays the results of the proximate analysis of lignin.

Table 1. Proximate Analysis of Isolated Lignin Samples

Sample	Moisture Content (%)	Volatile Matter (%)	Ash Content (%)	Fixed Carbon (%)
LSA2	2.42	19.63	0.12	77.83
LSA3	3.18	22.74	0.17	73.91
LCA3	3.48	21.56	0.15	74.81
LAA3	7.28	12.46	0.09	80.17

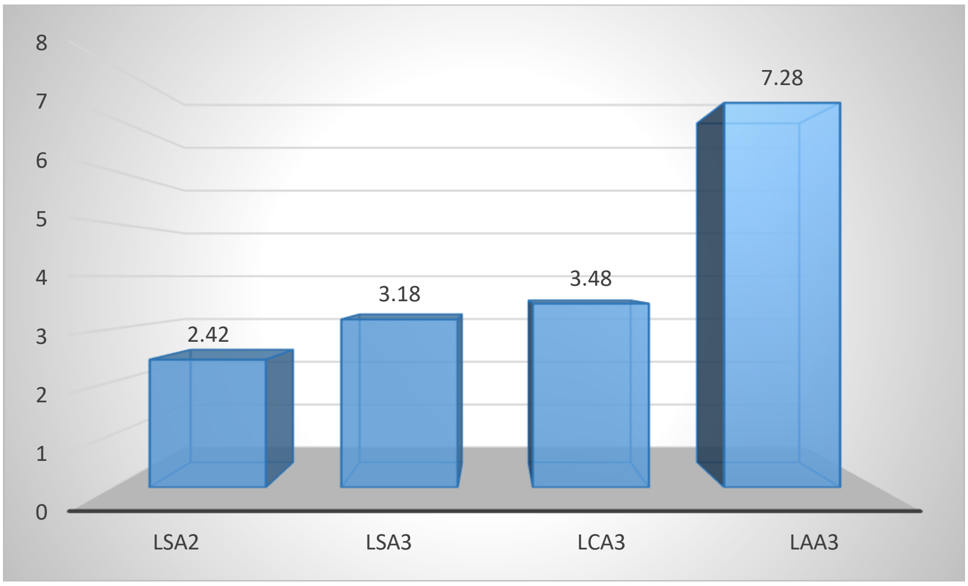

Figure 2: Moisture content of isolated lignin samples

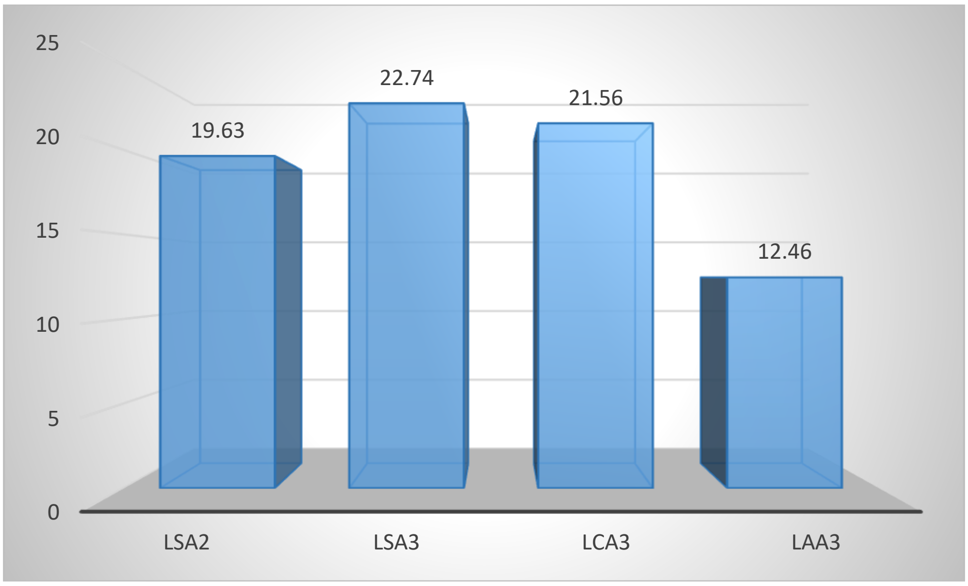

Figure 3: Volatile matter content of isolated lignin samples

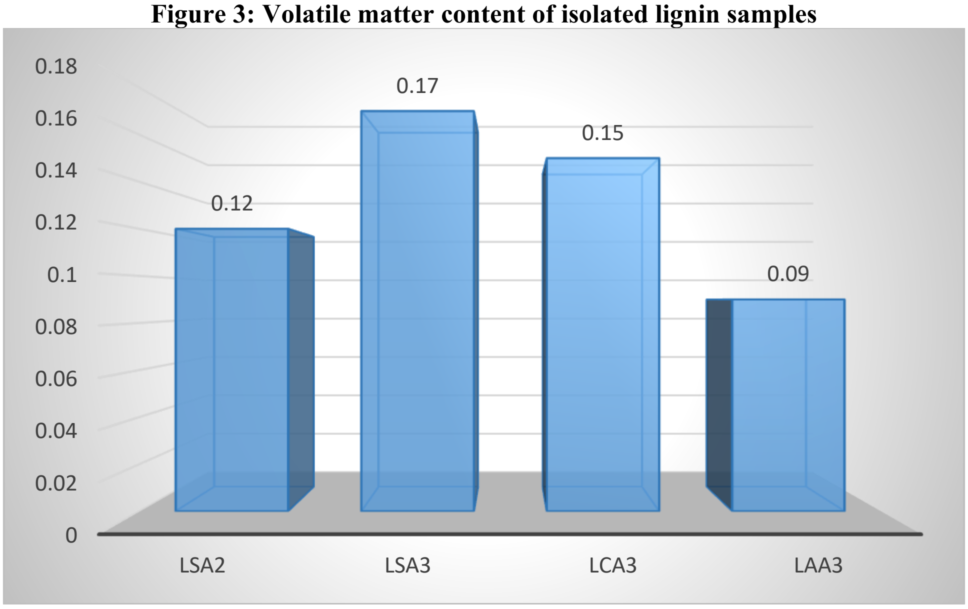

Figure 4: Ash content of isolated lignin samples

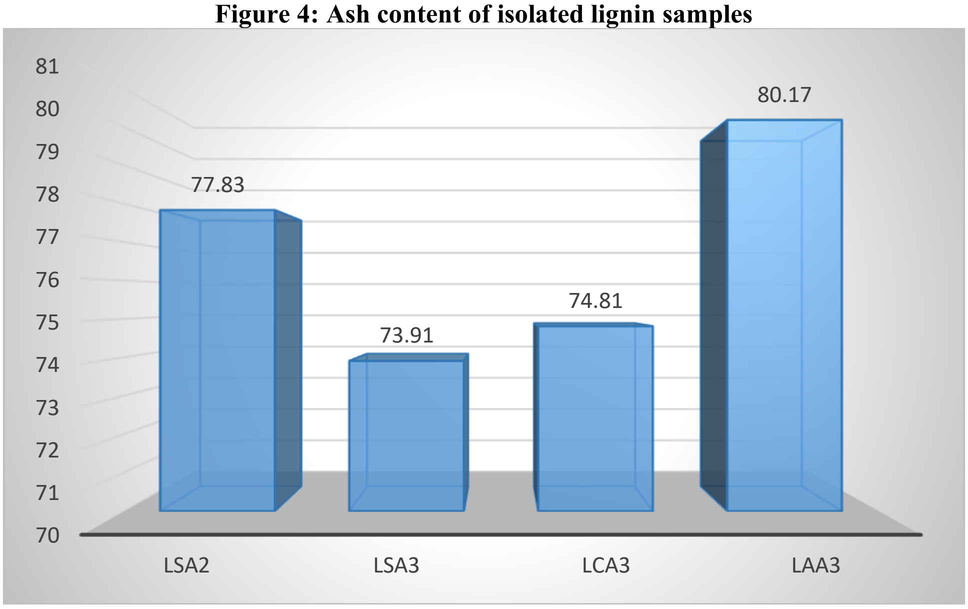

Figure 5: Fixed carbon content of isolated lignin samples

Based on the results, LSA2 was determined to have the lowest moisture content (2.42%), having been precipitated with sulfuric acid at pH 2. Depending on the acid used for precipitation, the amounts of volatile substances in the samples varied significantly. Due to its production with acetic acid at pH 3, the LSA3 sample had the greatest volatile matter level (22.74%), in contrast to the LAA3 sample, which had the lowest amount (12.46%). The ash percentages of the samples ranged from 0.09% to 0.17%, which is quite low. An ash concentration of just 0.09% was attained using LAA3. At 80.17 percent, LAA3's fixed carbon content was the highest of all the samples. LSA2 came in second, with a concentration of 77-83%.

Effect of Acid Type on Ultimate Analysis of Isolated Lignin

The results of the ultimate analysis are presented in Table 2.

Table 2. Ultimate Analysis of Isolated Lignin Samples

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulfur (%)
LSA2	59.18	6.08	0.39	30.96	3.39
LSA3	58.87	6.24	0.35	31.82	2.72
LCA3	71.86	4.26	0.64	20.58	2.66
LAA3	60.34	6.37	0.28	30.12	2.11

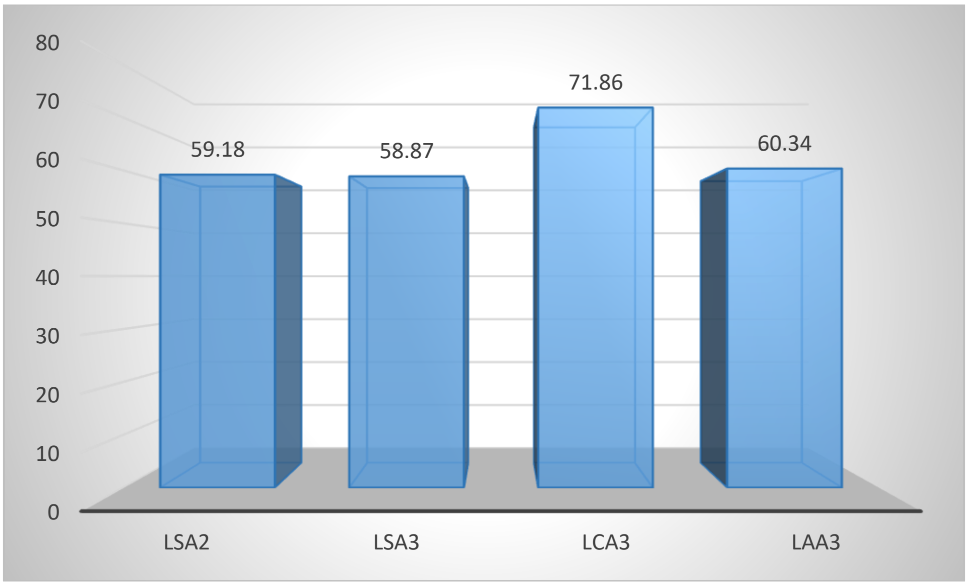

Figure 6: Carbon Content of Isolated Lignin Samples

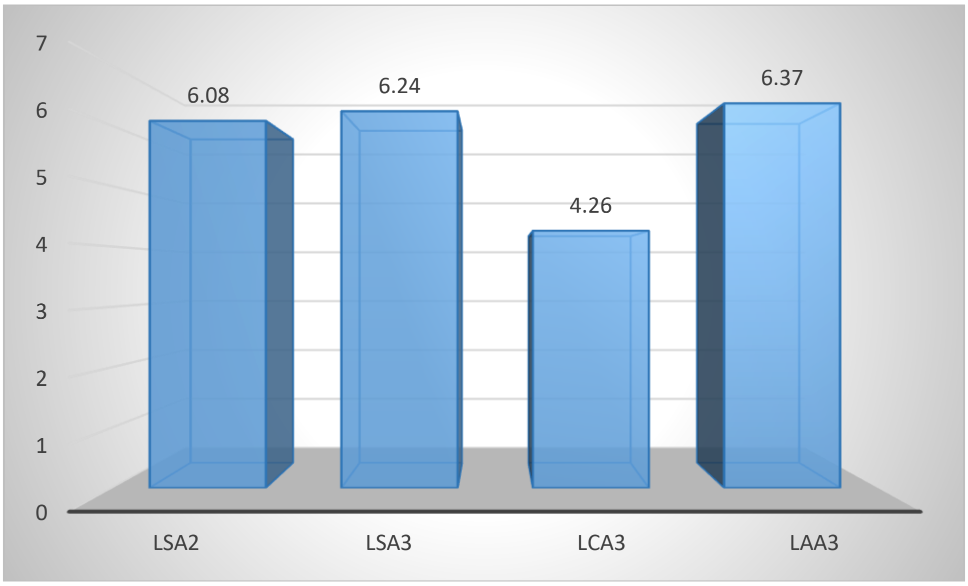

Figure 7: Hydrogen Content of Isolated Lignin Samples

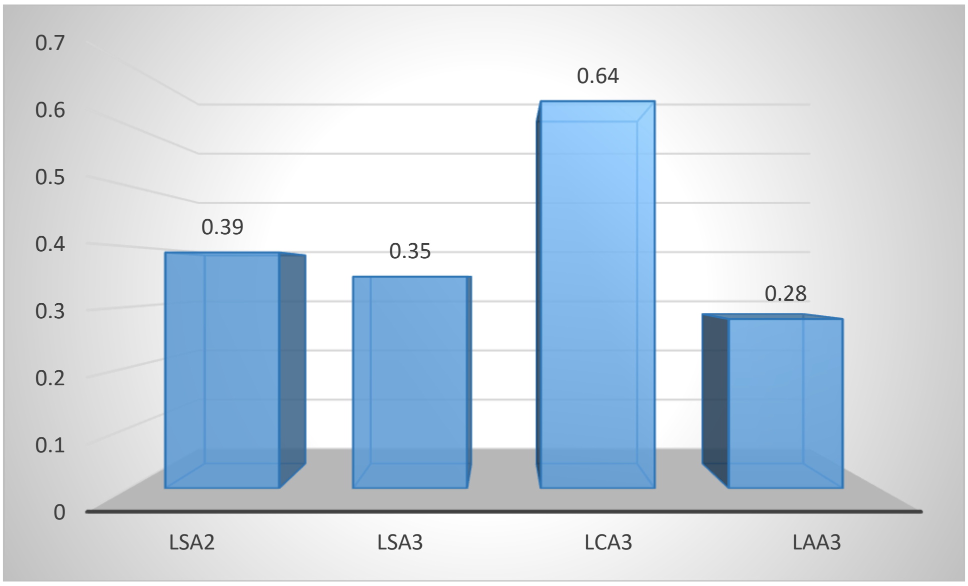

Figure 8: Nitrogen Content of Isolated Lignin Samples

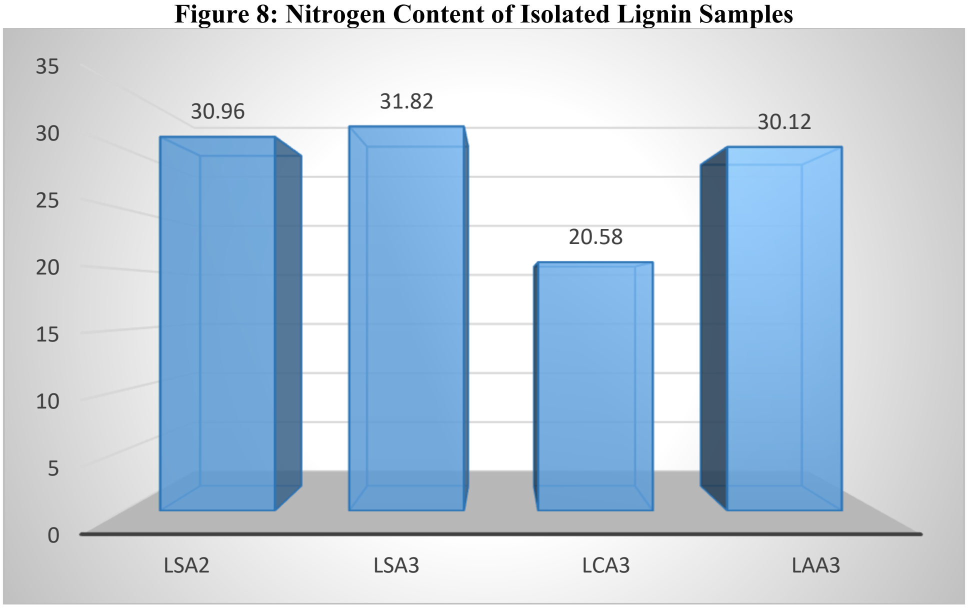

Figure 9: Oxygen Content of Isolated Lignin Samples

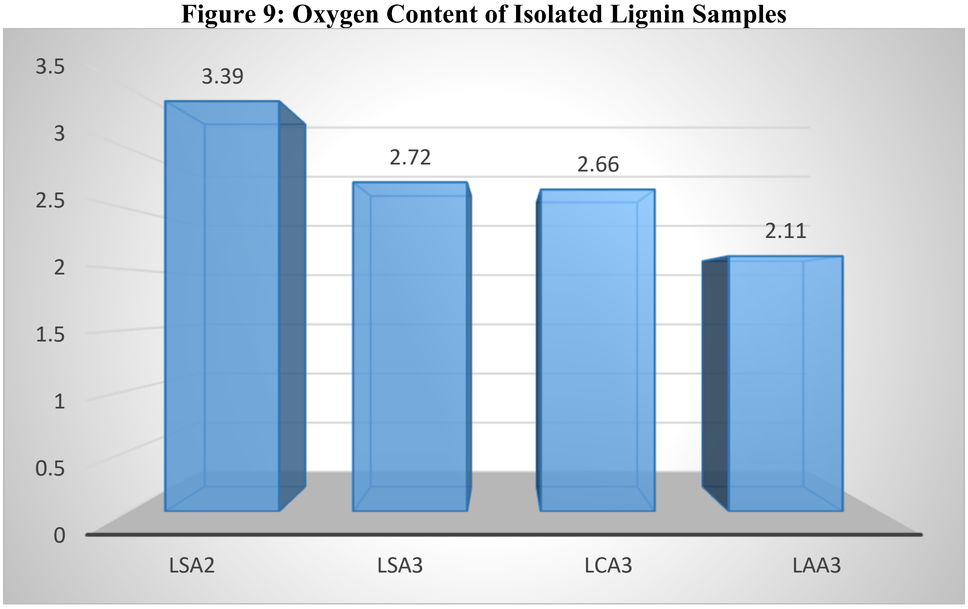

Figure 10: Sulfur Content of Isolated Lignin Samples

The results demonstrate that the elemental composition of lignin was significantly affected by the kind of acid used during precipitation. The sample with the greatest carbon content, at 71.86%, was LCA3, which was prepared using citric acid at pH 3. The percentage of hydrogen ranged from 4.26% to 6.37%. Los Angeles 3 had the most concentration of hydrogen at 6.37 percent, while Los Angeles 3 had the lowest. All of the lignin samples had relatively low nitrogen contents, ranging from 0.28% to 0.64%. Reduced production of nitrogen oxides (NO_x) during combustion makes air pollution levels with lower nitrogen concentrations more desirable. Cleaner combustion and less gaseous emissions were possible with the LAA3 sample because of its low nitrogen content. Oxygen concentrations varied between 20.58 and 31.82 percent. The LCA3 sample had the lowest oxygen content, whereas the LSA3 sample had the highest. A key environmental feature is sulphur content because of its involvement in sulphur oxide (SO_x) emissions during combustion. Sulphur levels were found to range from 2.11% to 3.39% in the current analysis, with LAA3 having the lowest value.

V. CONCLUSION

In order to make high-quality biomass briquettes, this research showed that kraft black liquor is a good lignin source. The physicochemical and fuel characteristics of the recovered lignin are greatly affected by the acid type utilised during precipitation, as the results shown. The lowest moisture content lignin was formed by sulfuric acid at a pH of 2, whereas the greatest fixed carbon content, lowest volatile matter content, and ash content were all products of acetic acid at a pH of 3. In a pH 3 solution of citric acid, the most carbon-rich lignin was produced, suggesting improved energy potential. In general, the lignin that was recovered showed some great fuel properties, which means it might be used for sustainable solid biofuels. In order to promote the valorisation of industrial waste and encourage the development of clean energy, the results show that acid-assisted lignin recovery from kraft black liquor is a sustainable and effective method for making high-quality briquettes.

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