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Review Paper

Soil Conditioner: Conversion of black Liquor Waste by Natural and Artificial Ammoxidation to value added product

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Abstract

Soil no longer sustains beneficial quality in compact; its fertile status has been altered, deteriorated, and destroyed, primarily attributable to massive use of conventional fertilizers, improper land use, rapid industrialization and deforestation. As a consequence of that soil became deficient in necessary carbon content, mineralized nutrient, and micronutrients. Inorganic fertilizer, used on a large scale and constant basis, causes many harmful effects on the environment, leading to soil erosion and leaching problems. Hence, there is a need of materials with a slow-nitrogen releasing effects, in huge quantity and quality to combat all these losses. Lignin is a major precursor of soil humic substances and source of plant nutrient capable of acting as slow-release fertilizer, if enriched with nitrogen by converting it to a suitable form. The richest source of lignin is black liquor (BL) a waste product obtained from pulp and paper industries in huge quantity. The conventional methods adopted by these industries for the recovery and disposal of lignin and lignin derivatives in black liquor causes air pollution. Further such installations are unaffordable for small non-wood mills, which are in need of value added products from BL. Preparation of soil conditioner from BL, could be the solution to above said problems. The objective here is to explore the field of lignin research to utilize Kraft lignin as a feedstock for production of soil conditioner, both by biological and chemical pathways. Present paper reviews the advances taking place in both natural and artificial ammoxidation methods of conversion of lignin to soil conditioner with the aim, to use black liquor waste completely in both higher molar mass fraction (HMMF) and lower molar mass fraction (LMMF). The key parameters influencing the processes were identified and reported.

Keywords: Lignin transformation, humus, microbes, artificial ammoxidation process.

Introduction

Problems related to soil have been intensified in the last two decades, demands immediate attention and remedies. Progressive deforestation and industrialization increases soil erosion and desertification, which are advancing at an alarming level, particularly affecting Asia and Africa, where they are spreading at an annual rate of 10.400 (km^2)[1] and reaching many parts of the world. Use of inorganic fertilizers acting as catalyst, magnifying the soil associated problems, affecting environment still further. All these malpractices are changing physico-chemical properties of soil speedily, and depriving the surface soil from mineralized nutrient, stored organic carbon and essential humus substances, which forms building blocks of green vegetation.

The most common practice in agriculture is to improve the soil structure is by application of organic matter to form most stable humus fractions[2]. But it is very difficult to avail both desired quality and quantity of organic matter substantially, to make compensation for the lost carbon rapidly. In nature considerable time is needed for the formation of such high-grade stable humus[3,4]. Lignin forms basis for humus formation and its resistant organic structure facilitates humus formation, therefore lignin based fertilizer could be the solution in future because of its abundant source in the form of byproduct, black liquor (BL) obtained from pulp and paper industries in huge quantity[5-7].

In the present scenario of lignin utilization through combustion in recovery boiler, is not very satisfactory as this method is costly, not environmental friendly, further such practices are, unprofitable for small non-wood mills[8,9]. A cost-effective and pollution free, disposal alternative would be, land use of black liquor as soil amendment to replace the existing recovery process[10]. Black liquor contains organic substances such as polysaccharides and lignin. A beneficial fraction of inorganic nutrients such as K, Ca, Mg, Zn and Cu etc., along with relatively low or undetectable concentration of heavy metals fractions are also present in BL. Kraft pulp shows increasing trend of production, in the last two decades, which consequently has also increased generation of lignin globally[11].

Literature survey revealed that, the important properties of lignin and its application as carrier of fertilizers were identified first by Liao Jun-he[12]. Thereafter, there is explosion of research in this particular era from the last 5-10 years. Li Yang-Jie et al reported that lignin should be widely popularized as slow release fertilizer, which will provide comparatively inexpensive approach to reduce the cost of agriculture and forestry at the same time cut short the pollution burden due to use of chemical fertilizer[13].

The dominant Kraft process accounts to 85% of total lignin production, worldwide. Lignin, the giant macromolecule is fractionated in the pulping process to various molecular mass fractions. Complete utilization of BL is important for sustainable development, with this aim; the present paper investigates ammoxidation processes of conversion of lignin to soil conditioner by both biological and chemical pathways. The natural and artificial methods of conversion of lignin, using both lower molar mass fraction (LMMF) and higher molar mass fraction (HMMF) were discussed. The key parameters influencing the processes were identified and reported.

Precipitation of black liquor

Direct application of Kraft BL to the soil may results into, undesirable side effects. Hence, isolation of lignin is preferred generally, and done by acid precipitation method for recovery[14-20].

After precipitation, two phases are obtained, as given in figure-1, the solid residue is recovered as higher molar mass fraction (HMMF) of lignin and the filtrate, which is in liquid phase contains, lower molar mass fraction (LMMF) of lignin, along with other material, which is biodegradable. This recovered lignin can be processed further for getting soil conditioner more safely, effectively.

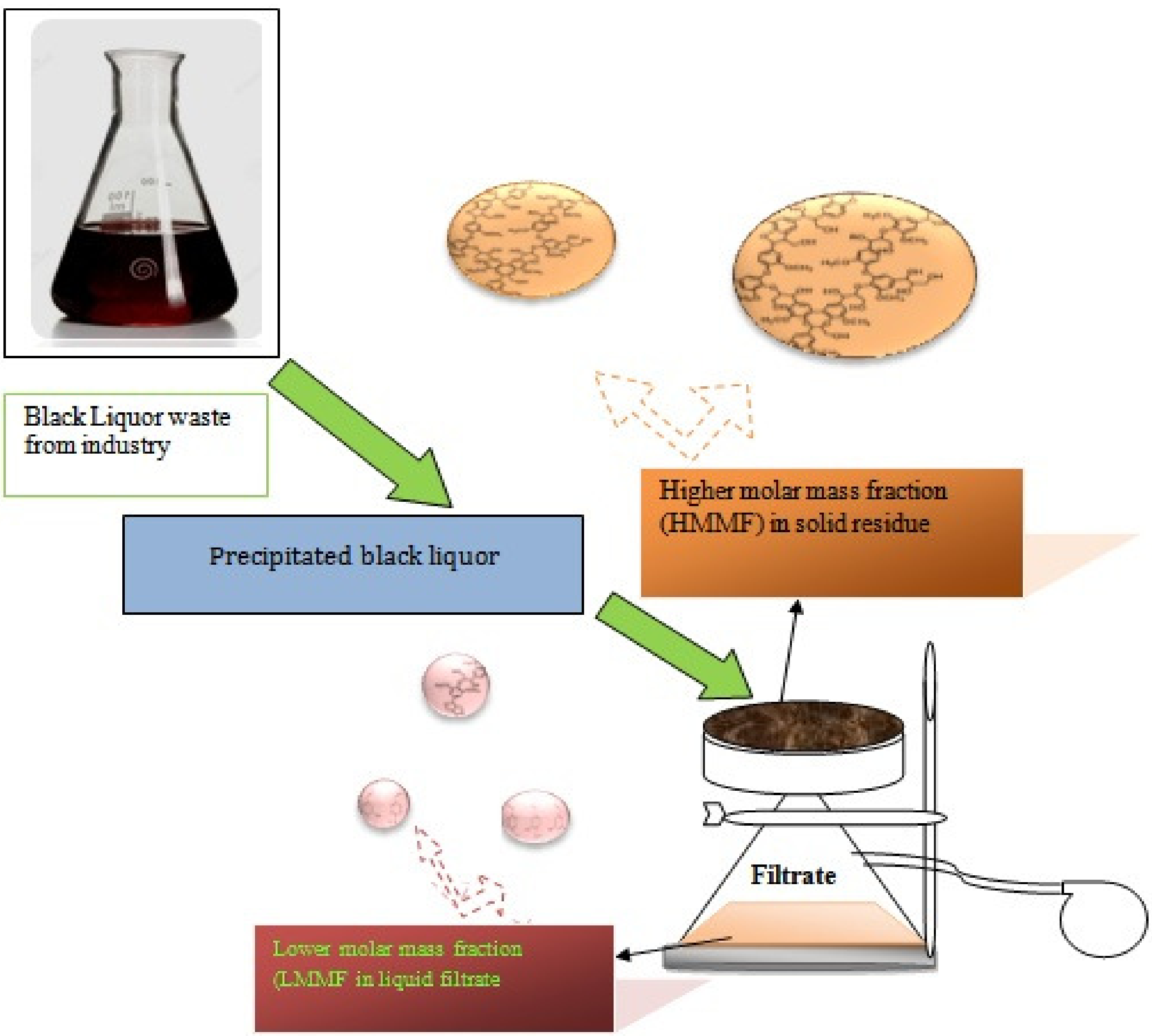

Figure-1
Precipitation of black liquor to two phases, higher molar mass fraction (HMMF) and lower molar mass fraction (LMMF) of lignin

Limitation of existing conversion processes

In nature, humification process transforms lignin continuously to humic material in top soil, but it takes years together to do so because of its highly branched macromolecular, plant derived origin. This process inadequate to fulfill the present requirement of humus matter, hence it becomes mandatory to search for other alternatives. Further lignin cannot be solely applied to the soil, as it hardly contains any nitrogen and requires additional application of a suitable nitrogen source. Hence, efforts are made in various ways, in the last two decades for modification of industrial lignin, based on which the processes can be broadly classified as mixing process, coating process, and pyrolysis process, The mixing method of manufacturing soil conditioner composed of mixing decontaminated manure and Bacillus spore, and lignin material optionally one or more of N-compounds. Zeng, Zhaoxiang had utilized BL directly to get fertilizer by using flocculating agent[21,22]. Black liquor is treated with a surface active polymeric, coagulant agent and then mixed with the phosphoric acid from the phosphate containing material[23]. BL is used to obtain low organic- K fertilizer or mixed with other fertilizers like NP, KZn, FeB to obtain composite fertilizer (24). Coating process is another way of using lignin as a coating media on mineral fertilizer. According to M. C. Garcia, J. A. Diez, at. el., major fraction of lignin can be used in a controlled-release fertilizer coating, by adding linseed oil as a sealing agent[25]. Process of pyrolysis, uses a chemical reaction for making organic slow release nitrogenous fertilizers from pyrolysis products of BL[26].

In all the above processes, the chemical species required to be added physically, and in the pyrolysis process although chemical reactions are involved, but due to refractory nature of lignin very little amount of nitrogen is incorporated into the polymeric structure of lignin, further considerable leaching of nitrogen occurs.

Ammoxidation Process

Looking at the limitations of above the processes, it can be said that lignin being more refractory than cellulose, the general process must be oxidative in nature. Thereby resulting in an increased carboxyl acid content of finished product, by microorganisms or chemical conversion pathways, both the processes may show considerable differences in humification data (27-30). Schematic representations of principle of natural and artificial processes are given in figure-2. Ammoxidation of organic matter containing lignin structures can thus be described as accelerated natural humification; the process is merely transferred into a petri-dish or a chemical reactor, using primarily Kraft lignin from the pulping industry.

Natural ammoxidation (humification): Natural process which takes place in the top soil requires long conversion time, owing to resistant highly branched biopolymer lignin. The important steps involved in biological transformation of lignin to humic matter are given in figure-2[27-29]. The process of pulping fractures the complex, high molar mass of lignin molecules into low molar mass fractions and solubilise them into alkali. After precipitation of BL, the residue contains bio refractory lignin (HMMF) but the filtrate contains lignin fractions, which are prone to biodegradation, preferably bellow pH 9.5, because of fractured matrix[31].

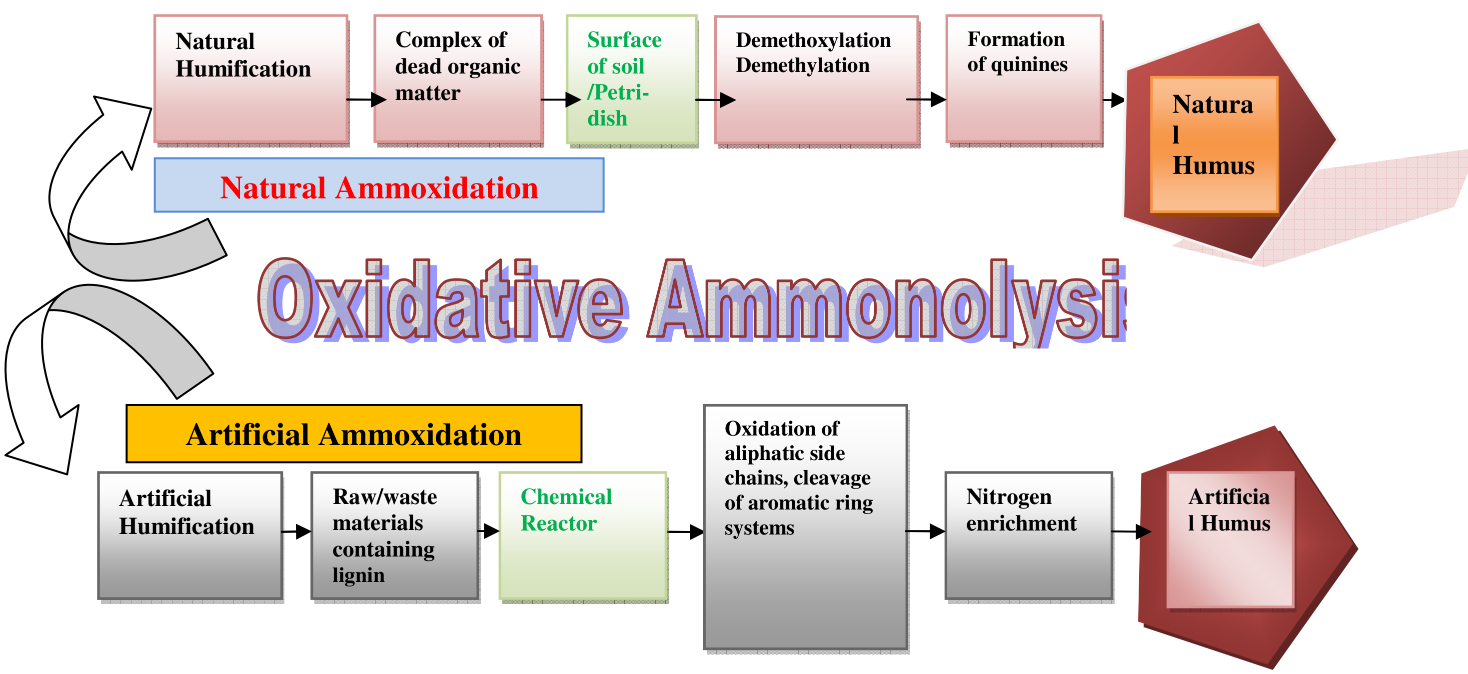

Figure-2
Oxidative ammonolysis is the main principle for natural and artificial humus formation (27)

The huge amount of filtrate which is available contains lignin and lignin related compounds and LMMF along with rich source of simple sugars, obtained from of higher carbohydrate groups and mixture of inorganic salts including sodium sulphate, sodium carbonate, and very little fraction of minerals, as investigated by Sahoo et. al.[32]. The literature study revealed that there is evidence for existing certain microorganisms that are capable of synthesizing humus precursors within the cell from simple carbohydrate substrates, such as spp. Aspergillus, Penicillium, and Tricoderma are the predominant fungal genera growing on simple carbon source[33]. Aspergillus spp. has a high lignin-degrading capacity[31]. The oxidative reaction imposed by fungal species is non-specific, cleaves aromatic rings and reduces methoxyl, phenolic and aliphatic structure of lignin to new carbonyl groups[27]. With glucose as sole carbon source, the culture media can give a brown organic residue which closely resembles natural soil humic matter. Further these microorganisms are capable of converting inorganic nitrogen available in the nutrient medium to organic nitrogen. The important parameters that may influence the biochemical conversion process includes the substrate molecule status, C/N ratio (nitrogen has to be supplied additionally to get desired C/N ratio in the range 21-40), types of microbes (fungi, basidiomycetes, actinomyetes, and few bacteria), temperature, pH, period of incubation and condition[34,35].

Artificial ammoxidation (humification): It has been found that Kraft lignin can be converted into artificial humic substances (organo-mineralic fertilizers) by ammoxidation process to produce slow release nitrogen fertilizer by chemical pathway using transformation given in figure-2[36,37].

Artificial ammoxidation of organic lignin structures is a transformed form of natural humification, using the special reactor and Kraft lignin waste materials from the paper industry.

This method was first introduced by Franz and Palm for N-enrichment of technical lignin. For high nitrogen content, oxidative ammonolysis in the past has been done exclusive at high pressures and temperatures. The important oxidizing agents were air, oxygen, potassium permanganate, and nitric acid[38-41]. The reactive agents in oxidative ammoxidation are oxygen (anionic radicals) and ammonia, which are responsible for the degradation of lignin macromolecules, the cleavage of aromatic ring units, and the final incorporation of nitrogen into these structures. The nitrogen bonds of resulting products can be classified into three types as ammonia groups (short span available), amide groups (mid span available), and groups with strong organic nitrogen (long span available) available to plants species[42]. While conventional ammoxidation require several hours to complete the reaction, time can be reduced to three hours by carring out the process at temperature 100^0C, aq. ammonia concentrate of 8 wt% and using lignin in acidic environment. Many processes were further developed to give acceptable level of nitrogen for its use as slow releasing fertilizer/ soil conditioner as found by Marvin Weil *at. el.* and other co-workers with the sole efforts to reduce time and temperature further[43,44]. In today's ammoxidation process of lignin time and pressure has been reduced significantly by incorporating more nitrogen in the finished product. When H_2O_2 is used as oxidizing agent encouraging results were obtained at atmospheric pressure, although rise in temperature makes the ammonization reaction speedy, but causes degradation of hydrogen peroxide and thereby retards the process significantly[45].

Zuniga[46] studied catalytic action of transitional metal elements such as copper (II), manganese, iron (II), molybdenum, on ammoxidation process; alkaline lignin was used along with hydrogen peroxide as oxidizer. Similar results were reported by other workers including Jiang Qi-Pei, Felipe Ramirez-Cano *at. el*.[47-50].

Field application of ammoxidised products

Many applications of ammoxidised products of lignin have been investigated in pot experiments by several research workers. Results from pot experiment grown rice and maize and corn pot test in which N-lignin was used as a controlled release material of urea, showed that a little dosage of N-lignin could not only increase biomass in evidence, but also improve nitrogen-utilized efficiency at a large degree[51,52]. Investigations were also done to preserve tropical rainforest by using nitro-fertilizer from lignin[53]. Xiao C. *at. el.* found applicability of lignin based fertilizer to improve aggregation and chemical properties of soil in the fields, and also play role as organo-mineral fertilizers in horticulture, organic farming[54,55]. The quality of humus produced by BL is similar to waste produced from mushroom production[56]. Wide applications of lignin based fertilizers have been achieved in many pot and field experiments successfully as cited in literature[57,58].

Conclusions

Based on all these studies, it can be concluded that Kraft black liquor can be completely used for the preparation of soil conditioner. Thus, after precipitation, the huge amount of filtrate generated can be used by microbes (fungi, basidiomycetes actinomyetes, and few bacteria) for obtaining humus material naturally (14, 34, 35, 59). While chemical conversion of more resistant, solid residue can be achieved by artificial ammoxidation to soil conditioner (60, 61). Therefore, it can be said that by the process of ammoxidation, both the solid and liquid phases of BL can be effectively converted to soil conditioner. The possible, ideal green system closer that could be achieved is represented schematically in figure-3.

These processes may be capable of combating the losses attributed to soil erosion, in reasonable time span and comparatively at fewer expenses, as BL waste is cheaply available. Hence, these methods may prove efficient for small to medium scale pulp and paper industry and able to reduce the load on recovery boilers in large scale paper industry. These processes could assist in curtailing the massive use of fertilizers. But such preparations are more limited to laboratory scale only for commercial application; dedicated efforts, attention and scientific research are desired to attain the final destination.

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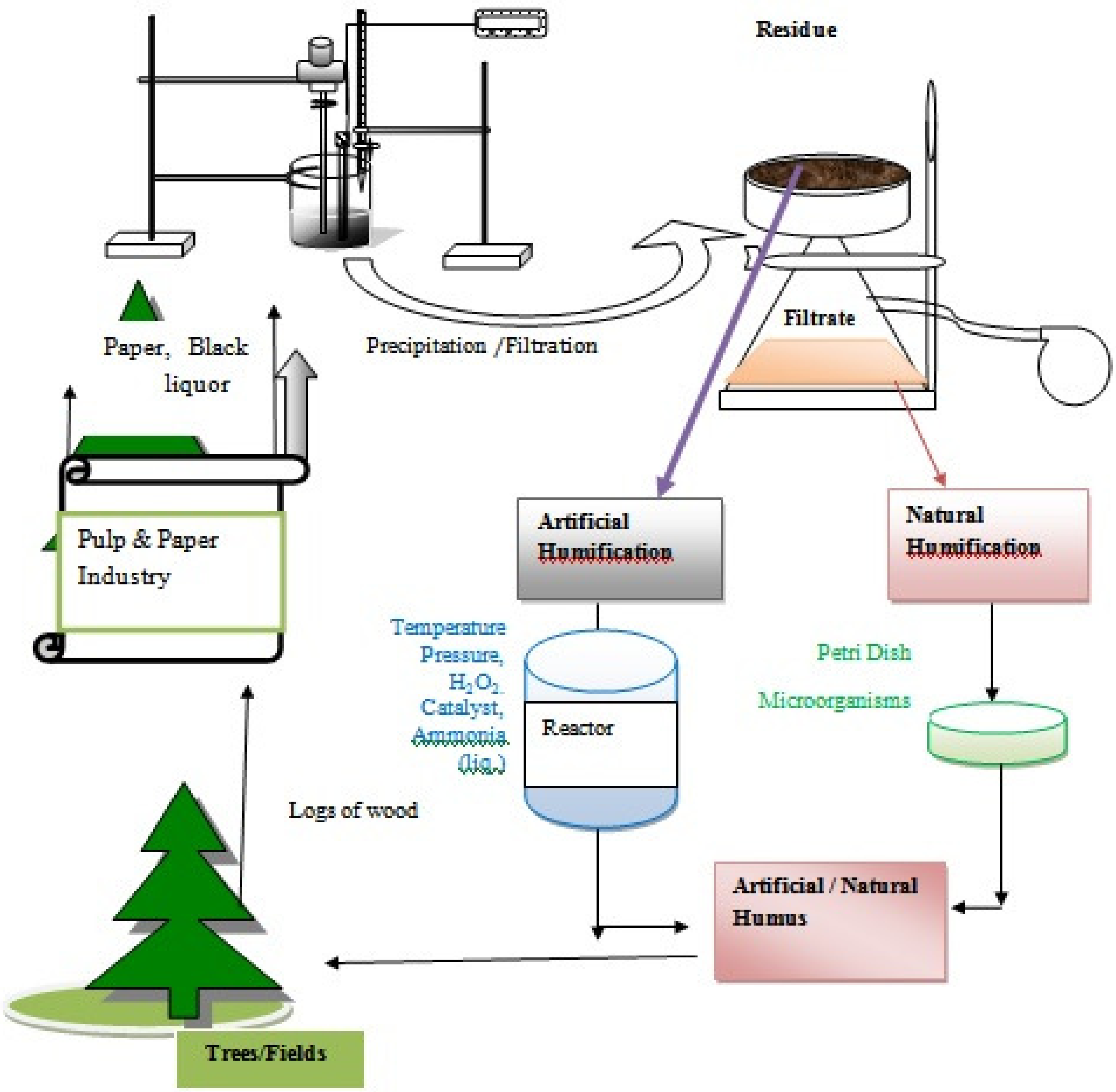

Figure-3
Ideal, green system closure, by converting black liquor waste to soil conditioner by natural and artificial ammoxidation

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