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A Study on the Dynamics of Black Liquor Droplets in Chemical Recovery Boilers

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Abstract – Black liquor is a by-product of the paper pulping operation. It is a diverse combination of organic and inorganic chemicals all of which provide chemical meaning and resources. The black liquor is concentrated at a concentration of about 60-85% of solids, and is shot into a recovery boiler with these two amounts. The black liquor is poured in the boiler in the shape of gout, which is sprinkled in the furnace atmosphere. The droplet is then dried, removed, and burned in series before coalescing with the smelt on the rim. The formulation of these processes during motions of the black liquor droplet is very complicated and, in this paper, we try, by observing the pyrolysis of dry-black liquor solids in a muffle furnace and simulating the weight loss during the despoliation period. At temperatures between 973 and 1274 K and for the period of residence between 30 and 180 s, experiments were carried out. A single reaction, which gives gaseous volatility and carbon, is used for the kinetic design of dry black liquor solids. The single reaction model suggested is smelled and by utilizing the two-dimensional non-linear regression algorithm, the best values of kinetic parameters are found: activation energy and Arrhenius constant. The results show a strong consensus among forecast and test details.

Keywords – Black Liquor, Chemical Recovery, Boilers

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INTRODUCTION

There are two major features of the black liquor recovery boiler. The heat energy released when the organic ingredients of black liquor is burnt in the furnace, on the one side, produces steam and the reclaim boiler acts like a steam boiler on the other. In the other side, pulp-diegetic compounds, sulfur and sodium, are collected from the black liquor and are then used as a chemical reactor by the recovery boiler. This dual purpose renders the construction of a rehabilitation boiler very difficult and complicates the operation of a boiler even more than the operation of traditional fuels, for instance.

The recapture boiler is a special construction as seen as a chemical reactor. In the regeneration boiler furnace, several physiochemical processes are performed in the same room and at the same time:

- air ingestion and furnace gas mixture
- feed and disperse black liquor into droplets
- drying of droplets of black liquor
- black spirit and pyrolysis gas combustion

- gasification a residual burning
- sulfide elimination to sulfide liquor compounds -
- Tap molten salt from the bottom of the furnace composed of sodium sulfide and sodium carbonate

Moreover, as a side effect, more or less unwanted:

- Sodium and sulfur compounds (as well as chlorine and potassium compounds in smaller measure) and vapor and fumes flowing through the roof of the flue gas oven.

The recovery kilns were traditionally planned and run on the basis of realistic and observational knowledge from full-scale recovery kilns rather than on the basis of comprehensive data on the processed physicochemical phenomena. But it's going to improve this scenario. In recent times a number of research labs have provided large numbers of entirely modern, foundational knowledge regarding recovery furnace processes.

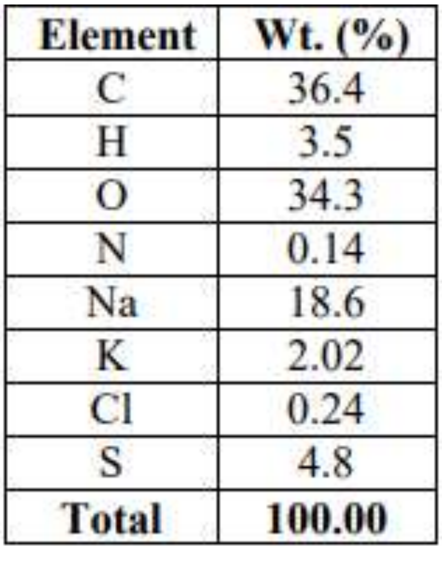
BLACK LIQUOR

Black liquor incorporates both the herbal and inorganic products of great value (Saw et al., 2009). It is a dense, dark brown liquid with a viscous effect. Per ton is formed with approximately 1 1/15 tons of dry black liquor solids or approximately 10 - 15 tons of poor black liquor with roughly two thirds organic and one third inorganic (10 - 18 percent of dissolved solidi's depending on the degree of dilution during washing). In a rehabilitation boiler, this mild black liquor is concentrated in 60 - 85% solids (Karlsson et al. 2013).

The organic material of black liquor is used for the manufacture of a high-pressure steam as a fuel in the recovery boiler, which is often used for power production. The heat content of black liquor solids (13-15 MJ/kg) is lower than fossil fuel. Nevertheless, the heat recovery effectiveness relies on the amount of black liquor and heat that the molten smelt drains from the heat boiler.

In Table 1 is provided the typical composition of the strong dry black liquor.

Table 1: Typical composition of dry BL solids



Element	Wt. (%)
C	36.4
H	3.5
O	34.3
N	0.14
Na	18.6
K	2.02
Cl	0.24
S	4.8
Total	**100.00**

RECOVERY BOILER

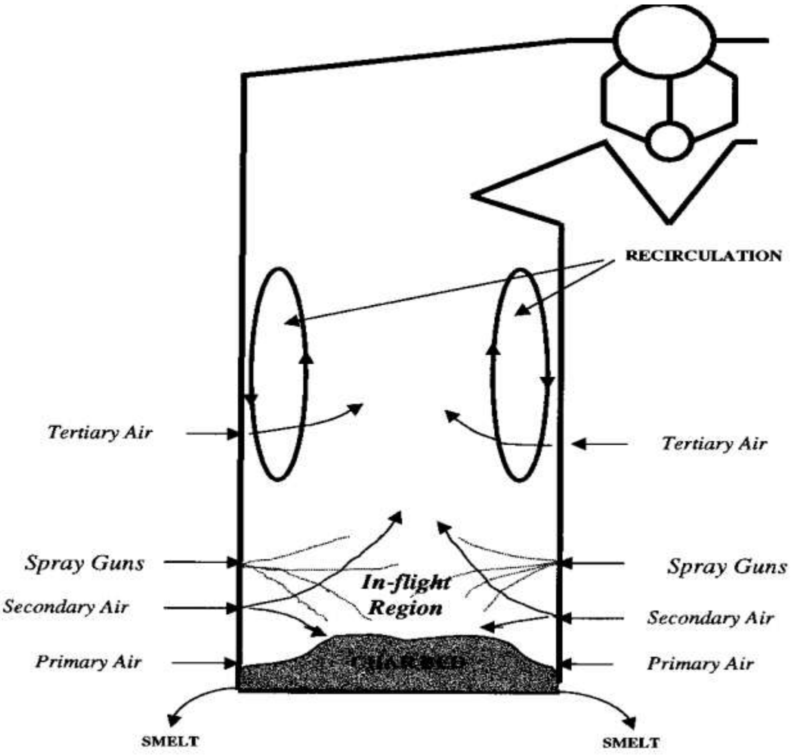


Figure 1: Schematic of recovery boiler furnace

Figure 1 shows the diagram of a standard remediation boiler. In the recovery boiler a black liquor is sprayed as gout in the injective pin, which is condensed in several impact evaporators (Johansson et al., 2009). These balls are provided from the bottom of the furnace approximately 5.5 m high. When in the heat gas ambience, the droplet undergoes three phases before reaching the bottom of the furnace (Miikulainen et al., 2004). The droplet lacks the humidity, which was referred to as a desiccation process (Whitty et al., 2008a) as soon as it is sprinkled inside the oven. The dried black liquor droplets undergo an increase in temperature as it descends which leads to a process of devolatilization (primarily a process of depolymerizing reactions). Not only does the particle drop its mass, but it is probably larger because of the swelling. The activity of the recovery furnace is influenced by such processes. Finally, particle 5 reaches the ground of the oven, known as the car-bed, where a combustion reaction is taking place. Combustion is the third step in which the remainder of the droplet begins to flame and reaches the char bed. The bed is composed of melted smelt and carbohydrate. The residue of the carbohydrate supplements the heat energy to reduce the sodium sulfate's response to carbohydrate to hold it molten. Smelt comprises mostly of all the inorganic chemicals charged in the cooking phase in the reactor.

In order to optimize the combustion of chars and volatiles, air is supplied for combustion in the boiler in the multi-tier port structure. The primary air supply is used for controlling the char bed's form and location. The side air monitors the orientation of the bed tip and combusts the volatiles of hydrocarbons. The tertiary air provides air for the operation of combustion. The bedtime is higher while the weather is higher before the whole carbon in the bed is burned and the bed is cooled due to extra air. The proposal for air supply is the following which relies on the proportion of the volatiles in BL solids in a typic three tier air dispersed boiler. The heat produced in a recovery boiler is generated with feed water and in its turn transformed by the economizer, boiler pipe banks, walls and superheaters into high-pressure steam to produce power and satisfy other requirements of process heat. The sun is absorbed by water-wall curtains as radiant heat.

REVIEW OF LITERATURE

Black liquor droplet formation

Aho et al. (2013) Studies on the effect of pine pyrolysis and pine cars on organic-bound metals have been performed. Selective leaching of the main ash forming elements in pine wood, including nitric, sulfuric, hydrochloric and oxalic acids, with various acids was carried out. No more substantial improvements were found in the chemical composition of biomass beyond metal removal. A beneficial impact on pyrolysis was the removal of metals (sodium, potassium, magnesium and calcium), which resulted in higher biomass oil, lower carbohydrates and oil production.

Studies on black liquor devolatilization

Savo et al. (2011) A first phase in testing the hypothesis was the laboratory scale analysis, which compares the combustion activity of various added amounts of biomass. A) At 900oC, the total black liquor content, 10% O2, was more than double the average of 1100oC, 3.3% O2. The study's observations are (a) b) At 900oC, the swelling decreased steadily, with the incorporation of more biomass.

Pyrolysis and kinetic parameters estimation

Lycksam et al. (2012) Using holographic interferometry, both the swelling of droppings and the speed of the gasses emitted during black liquor heating are measured. The pace was found several meters a second in the vicinity of the decline, but the contact with the air accompanying the exhaust gas soon decreased. After laser heating begins, the paths of the executed gas appear to lie near the path of the inbound laser light. However, after a while the gas explosion was more predictably emitted. The temperature profile of the gas that was expelled is therefore approximately estimated, although there are certain variations in the measured temperatures due to the comparatively low gassing temperature and the insufficiency of the gas composition at all times.

Char combustion

Engblom et al. (2012a) In the presence of a chemical reactive boundary plate, a statistical char-bed model was presented. Simulations were carried out for the char-burning studies of the Institute of Paper Science and Technology (IPST), with the following conclusions taken.

a) Boundary-layer responses consume oxygen which increases both gas phase and coal-bed temperature, having a net exothermic effect on the overall combustion.

b) Bulk gas oxygen contributes to carbon transformation, while gas phase reactant carbon transformation can take place entirely by gasification response.

c) Overall carbon conversion may be reduced either because of the direct impact of gas phase chemistry on boundary layers or because the combustion within the frontier layer influences the flow of mass across that layer.

EXPERIMENTS

Materials and Equipment

Black liquor, obtained in a nearby paper mill (around 60%) and applied as a thin foil in a stainless-steel tray, dried 24 hours in an oven at 378 K. The DBS is gathered as a flake and powdered to small pieces. A laboratory muffle furnace with digital temperature indicator cum control is used to conduct the pyrolysis of strong, dried black liquor samples.

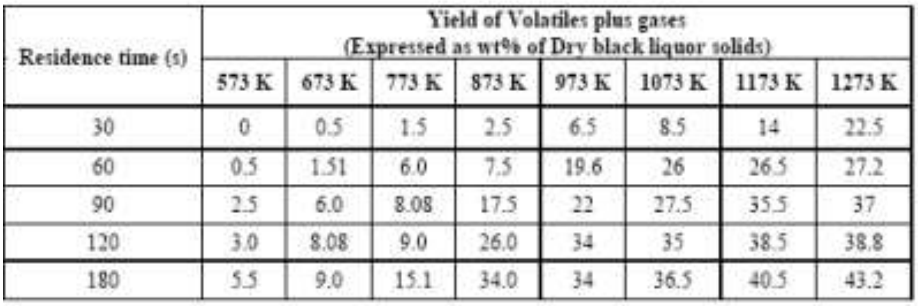
Experimental Procedure

The kinetic parameters for gaseous volatile releases of black liquor solids pyrolysis into the muffle furnace are determined by tests. The parameters are as follows:

- Initial temperature: 300 K ± 3 K room temp.
- Final range: 573 – 1273 K. Temperature.
- Period of holding (residence) until final temperature is reached: 30 to 180 s.

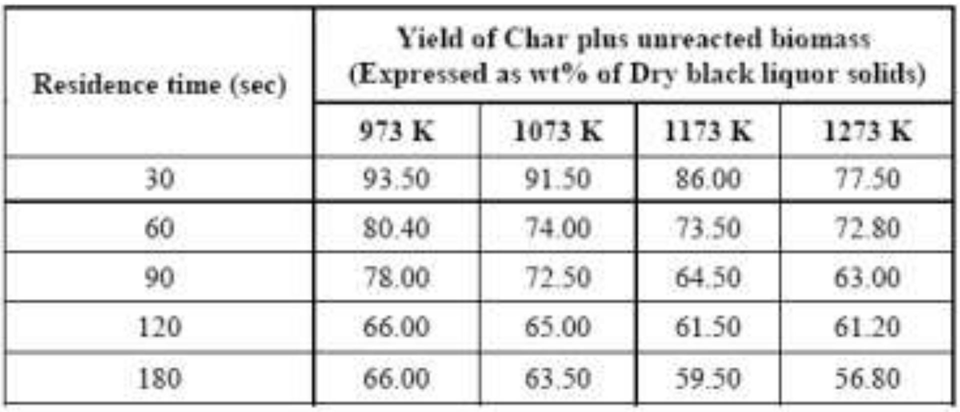
A predefined sample weight is taken in a silica crush and maintained in the oven for various periods of residence until the final temperature is reached. The crucible is measured at the conclusion of each trial to evaluate the yield of the released and carbohydrates. Most test runs are repeated to validate the values received. Tables 2 and 3 shows the representative performance of gaseous volatility and char for various dimensions of residence and temperature.

TABLE 2: Volatile Plus gas return experimental data on different times and temperatures of residence



Residence time (s)	Yield of Volatiles plus gases (Expressed as wt% of Dry black liquor solids)							
	573 K	673 K	773 K	873 K	973 K	1073 K	1173 K	1273 K
30	0	0.5	1.5	2.5	6.5	8.5	14	22.5
60	0.5	1.51	6.0	7.5	19.6	26	26.5	27.2
90	2.5	6.0	8.08	17.5	22	27.5	35.5	37
120	3.0	8.08	9.0	26.0	34	35	38.5	38.8
180	5.5	9.0	15.1	34.0	34	36.5	40.5	43.2

TABLE 3: Unreacted biomass yield in various times of residence and temperatures in terms of weight Percentage DBS experimental data on char plus



Residence time (sec)	Yield of Char plus unreacted biomass (Expressed as wt% of Dry black liquor solids)			
	973 K	1073 K	1173 K	1273 K
30	93.50	91.50	86.00	77.50
60	80.40	74.00	73.50	72.80
90	78.00	72.50	64.50	63.00
120	66.00	65.00	61.50	61.20
180	66.00	63.50	59.50	56.80

KINETIC MODELING

Solid dried black liquor Pyrolysis requires highly complicated reactions which results with a wide range of materials. It's incredibly challenging to develop an exact process for reaction and cinematic simulation of DBS pyrolysis. Kinetic parameters typically include energy activation, pre-exponential factor and reaction order describing mass loss rates. In order to build an appropriate pyrolysis reactor, it is important to consider the kinetics of pyrolysis. There has been a great deal of study in modelling pyrolysis kinetics for different organisms, leading in different periods to different reaction schemes. Mainly biomass from agricultural sources, as in this report, is the main subject of the majority of these researches. black liquor is the industrial waste. As such, the pyrolysis of dried black liquor solids is no literature. Our analysis uses the one-stage kinetic system of biomass pyrolyze as described below in Fig. 2. Here, DBS provides as the main pyrolysis materials volatile plus gases and char.

The test results would then be equipped with the kinetic equation in Equation 1.

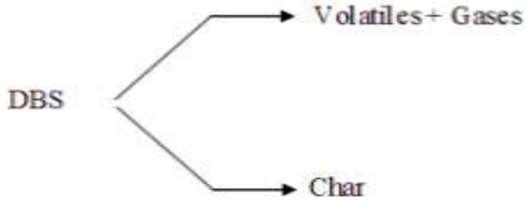


Figure 2: Kinetic system for solid dry black liquor (DBS)

$$\frac{dV_i}{dt} = k_i(V_i^* - V_i) \qquad (1)$$

The V_i range is the substance yield i at all times t, V*i is the ultimate value of V_i at high temperature and long residence period (determined as part of the fitting procedure with high conversion of the experimental data).

Here Ai is a pre-explosive element, activation energy for E_i, gas constant for R, and temperature for T. The rate of creation of a commodity is first ordered according to the disparity between the final yield and the quantity of that product that was generated before then. The film parameters for volatiles plus gasses and char are contained in the nonlinear regression algorithm of the two-dimensional surface fitting.

Estimation of Kinetic Parameters

The two-dimensional surface fitting non-linear regression algorithm as suggested by Xu and Kandiyohi has been calculated for kinetic parameters. By using this method, the quest path closest to the assumed initial value is observed and thus the algorithm cannot reduce the error to greater degree. We have therefore changed the initial algorithm in the last three stages. The algorithm changed is the following:

1) A pair of values of A and E are chosen initially randomly, and the next rough range is computed from two parameters

$$A_i = A_0 + \Delta A_0(1+\cos\theta_i)$$
$$E_i = E_0 + \Delta E_0(1+\sin\theta_i)$$

where, $\Delta A_0 = A_0 / N_1 ;\ \Delta E_0 = E_0 / N_2$ are the searching step lengths adjusted by changing the values of N1 and N2 .

2) Initially, $N_1 = 10.0$ and $N_2 = 10.0.$ $\theta_i = i(2\pi / N)$ is the searching direction $(i = 1, 2, ---, N)$

3) The eight points around the point of reference, for instance, is N = 8.

4) The residence time is calculated for each pair of kinetic parameters by Runge-fourth Kutta's order procedure for single phase reaction, at any reaction state specified by keeping temperature.

5) The hunt is done for the better match kinetic parameters by calculating the default error of each pair of kinetic parameters.

$$\delta_i = \frac{\sum_{j=1}^{M} \left| (V_j - V_{mj}) \right| / V_{mj}}{M}$$

RESULTS AND DISCUSSION

In accordance with temperature, Fig. 3 indicates a reduction of weight for dry black liquor samples. The number of chars reduces with a rise in temperature may be observed. The larger molecules in the remaining solids are broken down at higher temperatures to release smaller molecules, enriching the gaseous portion. Also, at elevated temperatures, cellulose is depolymerized. As a result, unpredictable plus gas supply is increasing with temperature rises. As compared to traditional biomass like sawdust, the reduction of weight of dry black liquor samples can be shown to be less because of the higher volume of inorganic compounds available for dry black liquor samples.

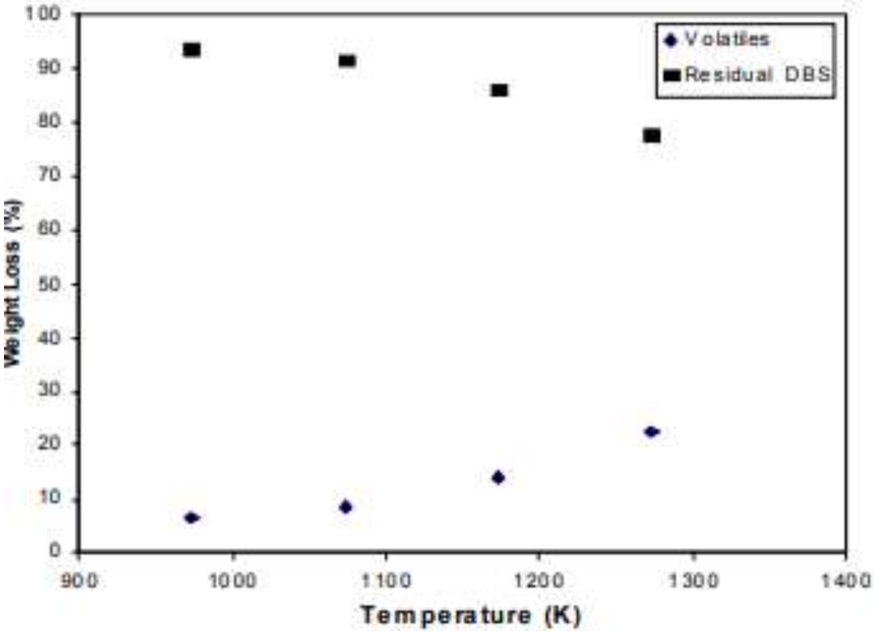


Figure 3: Weight loss Vs the Temperature curve residence period curve is 30 s.

For volatiles DBS plus gases, the best-fit kinetic parameters are calculated. DBS kinetics vary with temperature areas. From Table II the volatility of 573 – 873 K for a residence period of 30 s can be observed to be very restricted. Therefore, two zones A and B are considered to be simulations. The Temperature of zone A in the range of 973 K to 1073 K is from 1173 K to 1273 K in the range of zone B. A variety of simulation sets of initial frequency factor and activate energy values are performed to approximate kinetic parameters. As the simulation continues, the standard error is observed to decline, the minimum value is provided to a certain range of initial guess value, and then rises. The experimental value is then contrasted to the model estimation as seen in Fig. 4a and Fig. 5a for zones A and B of DBS volatiles, respectively, in order to detect the lowest standard error possible. Then a range with the lowest standard error is selected for kinetic parameters (i.e. frequency factor and active energy). Fig. 4b and Fig. 5b display the amount of iterations required for the frequency factor and energy activation which has a minimum error value for Area A and Area B.

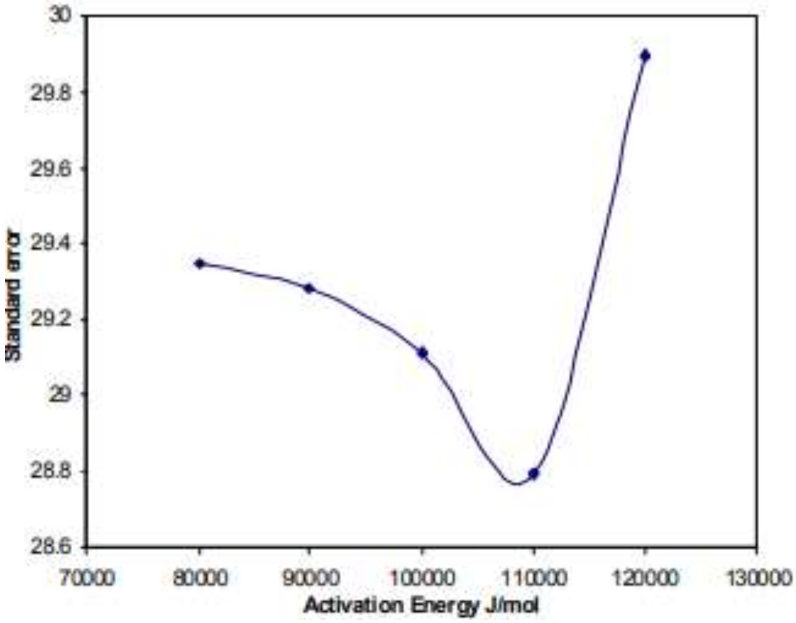


Figure 4a: Standard error versus energy activation (Arrhenius constant: 10000) at 973 K-1073 K Temperature range

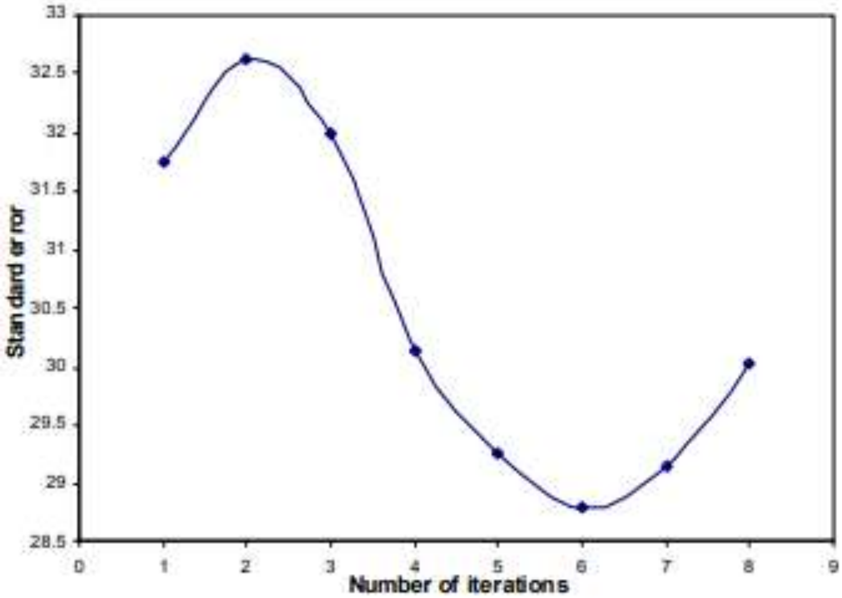


Figure 4b: Standard error Vs Iteration number of the 973 K-1073 K temperature range

Table 4 and Table 5 display the experimental and expected volatile gasses for black liquor solids for current frequency factor and activated energy levels with the lowest normal error values for zones A and B. Fig.6(a-d) illustrates the relation with new kinetic parameters of experimental data and simulation effects. The estimated values fit the full spectrum of experimental results provided very fairly.

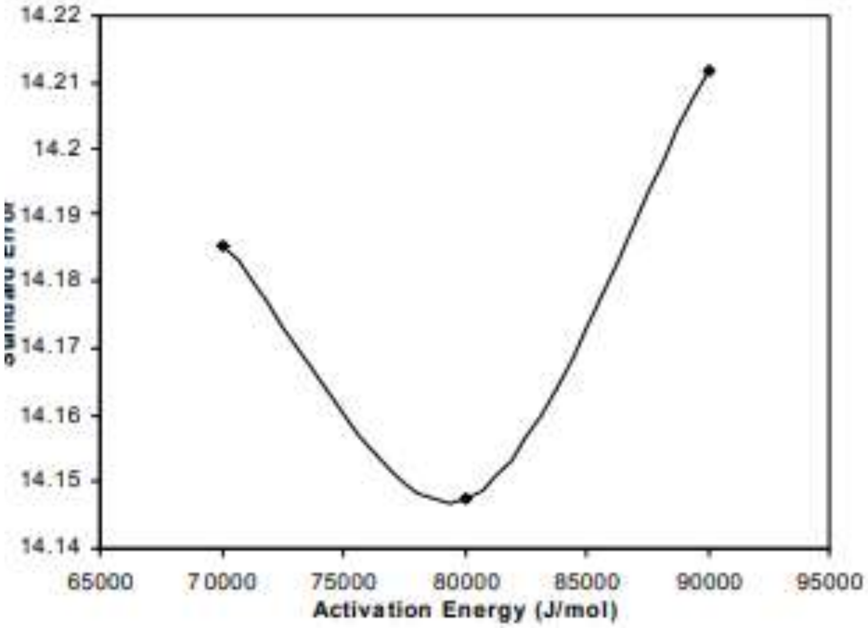


Figure 5a: Standard error vs activation energy in the temperature range 1173 K-1273 K (Arrhenius constant:10000)

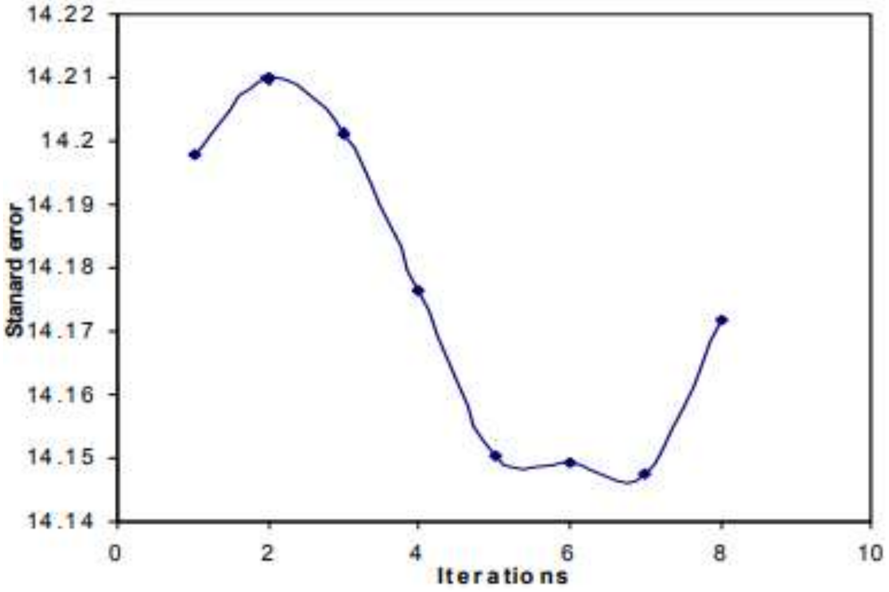


Figure 5b: Standard error Vs Iteration number of the 973 K-1073 K temperature range

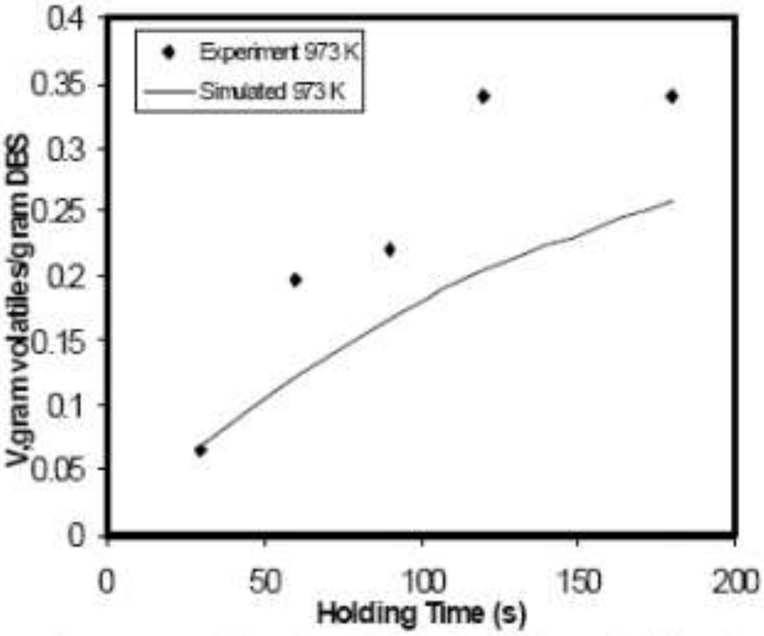


Figure 6a: Experiments 1 and simulated data on volatile Vs with a 973k keeping time

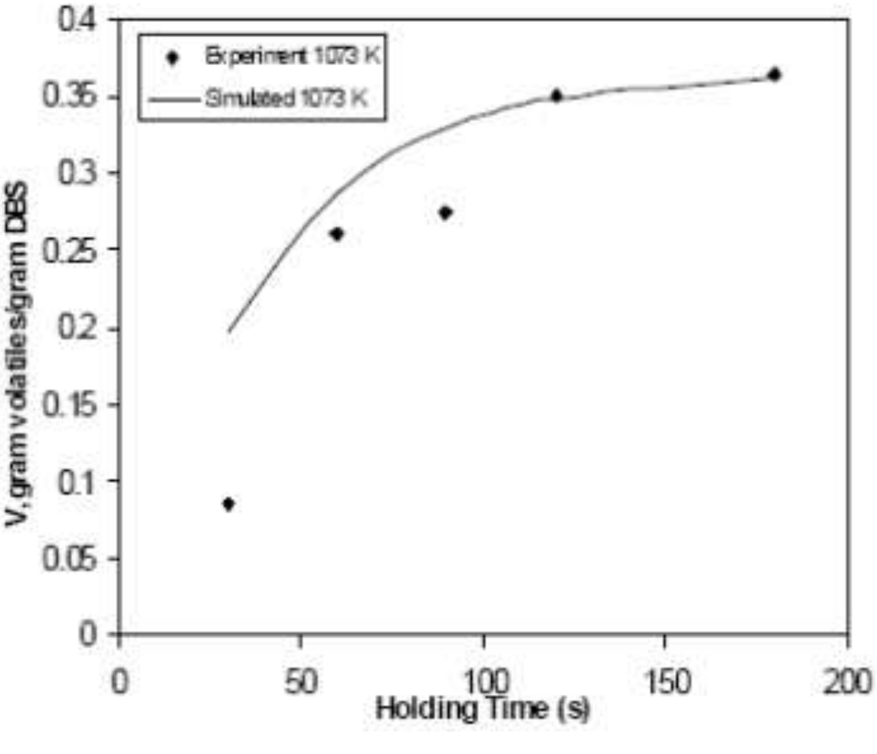


Figure 6b: The volatile Vs holding duration at 1073K was experimental and simulated results.

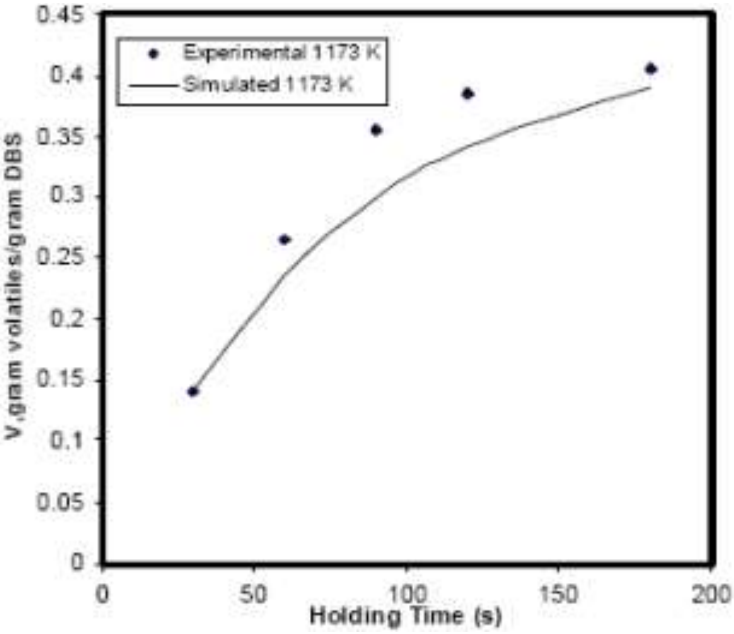


Figure 6c: Data from volatility versus time of repair at 1173k was experimental and simulated

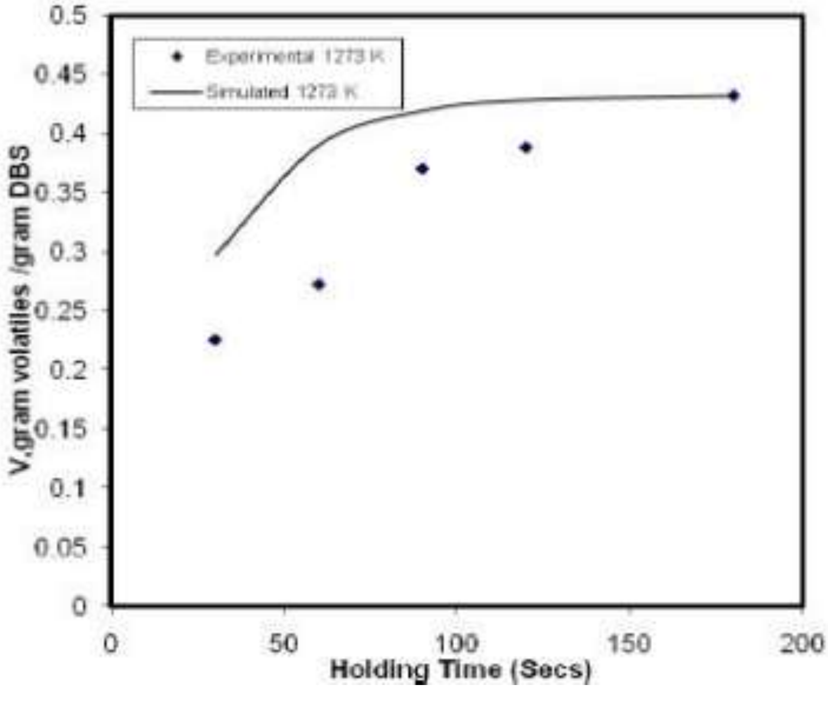
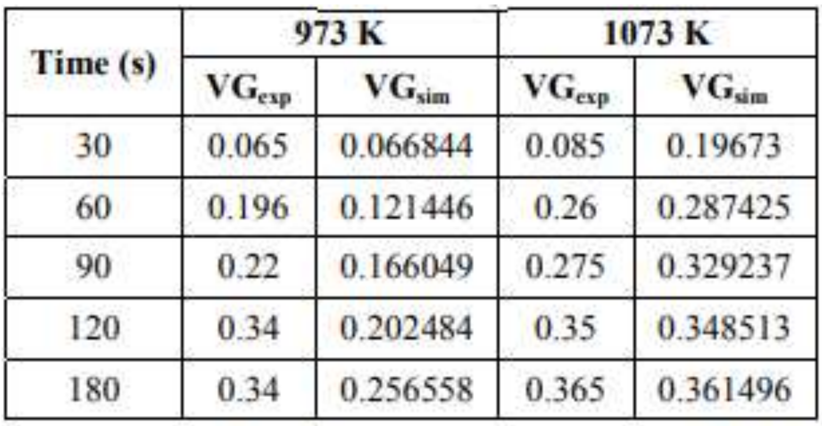


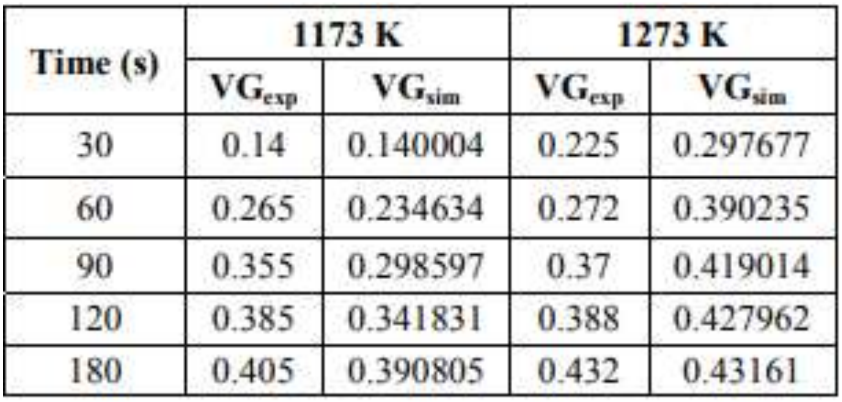
Figure 6d: Experimental and simulated volatile results against the keeping time at 1273k.

TABLE 4: Different residence times and temperatures yield volatile plus gases (“Initial Guess Values: A = 104 S-1, E = 80000 J/Mol, New Values: Anew = 112137 S-1, Enew = 116515 J/Mol, Δ =29.348777”)



Time (s)	973 K		1073 K	
	VG_{exp}	VG_{sim}	VG_{exp}	VG_{sim}
30	0.065	0.066844	0.085	0.19673
60	0.196	0.121446	0.26	0.287425
90	0.22	0.166049	0.275	0.329237
120	0.34	0.202484	0.35	0.348513
180	0.34	0.256558	0.365	0.361496

TABLE 5: Different residence times and temperatures yield volatile plus gases (“Initial Guess Values: A = 104 S-1, E = 80000 J/Mol, New Values: Anew= 114359 S-1, Enew = 135661 J/Mol, Δ =14.14737”)



Time (s)	1173 K		1273 K	
	VG_{exp}	VG_{sim}	VG_{exp}	VG_{sim}
30	0.14	0.140004	0.225	0.297677
60	0.265	0.234634	0.272	0.390235
90	0.355	0.298597	0.37	0.419014
120	0.385	0.341831	0.388	0.427962
180	0.405	0.390805	0.432	0.43161

CONCLUSIONS

This paper describes the research experiments carried out at different temperatures and residential periods of pyrolysis of black dried liquor solids. The kinetic system and the non-linear regression algorithm for the two-dimensional surface arrangement as illustrated were used for the analysis of the experimental data collected in two temperature zones. The kinetic parameters for both zones were determined and the contrast of test results with the expected data shows strong consistency. The value of kinetic parameters is found to increase marginally as zone temperature rises. The findings reported in this paper would hopefully help to predict the weight loss in a black liquor chemical recovery boiler during degradation of the black liquor droplets.

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