BIUST Research and Innovation Symposium 2017 (RDAIS 2017)
Botswana International University of Science and Technology
Palapye, Botswana, 12-14 June 2017

ISSN: 2521-229X
ISBN: 978-99968-0-608-7

Enhancement of the Pyrolysis Process Using Ultrasound

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***Abstract*— It has been estimated that Botswana has more than 200 billion tons of coal locked up in its underground reserves. The logistics for export purposes simply do not exist to get these vast resources to the markets. There has been huge efforts prove feasibility of develop plans to establish these logistics but to date there is still nothing forthcoming. On the other end of the spectrum there has been interest to develop and commercialize processes in which coal is converted into valuable products (e.g. via coal pyrolysis) which either have local markets or for which the export logistics already exist (or can easily be created).**

Sonochemistry can be utilized to enhance the coal pyrolysis process. In sonochemistry, ultrasound waves are applied to a liquid or liquid mixture to such an intensity that cavitation takes place. Cavity formation and collapse cause extreme local temperatures (>5000K) and pressures (>100bar) at extreme heating and cooling rates (109K/s). The hot spot theory is widely used to describe this phenomenon. Since chemical kinetics are directly influenced by pressure, temperature and heating/cooling rates, it follows that sonochemistry can be used enhance chemical processes and this has been shown to be true in many other industries (especially the medical industry). It is therefore reasonable to expect increased oil production yields and rates during the pyrolysis of coal as well and this would result in a better return on investment (ROI) for projects.

This project, which is still in its incipient stage, aims to determine the sonochemical parameters which will be conducive to the pyrolysis of coal. The kinetics of sonochemical pyrolysis reactions have been studied and these sonochemical principles have been used to establish a framework in which the project objectives can be met. These objectives include the formulation of a mathematical model for sonochemical pyrolysis, the design and construction of sonochemical pilot reactor and the subsequent testing and analysis using the pilot facility.

The experimental work will entail attachment of an ultrasonic transducer to a small desktop adiabatic batch reactor (able to contain 1000ml of raw material). The pressure and temperature of this reactor will be set to predetermined values before the experiment starts. The changes in pressure and temperature will be measured accurately and recorded together with product yields for various ultrasonic frequencies and intensities. Gas and vapour products will be sampled during the experiment and analysed while the liquid and solid products will be analysed after completion of the experiment. The experiment will be repeated for a range of operating conditions. The effect of ultrasonic frequency, intensity, temperature and pressure will be analysed, documented together with conclusions and recommendations.

Keywords—sonochemistry, sonolysis, pyrolysis, ultrasonic, cavitation, acoustic irradiaton, bubble dynamics, energy, fuel, oil

I. INTRODUCTION

It has long been a known fact that Botswana has more than 200 billion tons of coal. However, this vast amount of coal lies dormant underground since there is no way to transport significant amounts of it to a port for export purposes. The amount of coal consumed internally to generate power warrants only one coal mine in the whole of Botswana. It has therefore been the goal of many organisations to find alternative ways in which to utilise this coal economically. Many attempts have been made to prove feasibility of a new dedicated long haul railway line to both the Indian and Atlantic Oceans, but with no success to date. Others have ventured along power generation opportunities while yet others are looking into coal to liquid (CTL) projects. However, on a relatively small scale of implementation, such as is relevant to Botswana, there has been little success in proving feasibility to date.

Pyrolysis has been applied to coal and other forms of carbonaceous materials for many centuries to obtain high value energy products. Thermal decomposition of the raw material is achieved by applying heat in an oxygen free environment. Various regimes of pyrolysis have been developed over time and these cover applied temperature (below 400 °C, up to 600 °C and above 600 °C), heating rate (slow, medium, fast and flash pyrolysis), pressure (vacuum up to several atmospheres) and a wide range of catalytic processes.

Ultrasonic energy has been used successfully is other industries to enhance chemical reactions. Since pyrolysis also requires significant energy for the decomposition to take place, it can hypothesised that acoustic energy could equally be applied to achieve the same through sonolysis.

Sonochemistry is a mild, safe, and particularly green technology [13]. It accelerates chemical reactions and permits the use of less forcing conditions. It make a process more economical by the use of standard reagents and solvents and often reduces the number of synthetic steps required. It reduces any induction period with unwilling synthetic partners and initiates stubborn reactions while enhancing catalyst efficiency and radical reactions at the expenses of polar ones.

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II. SONOCHEMISTRY

A. *Chemical Kinetics*

Although we are concerned about amounts of material that react, amount of products that form and the rate at which they form (i.e. at a macroscopic level), this is driven by what happens on a molecular level. Collision of atoms with each other, energy levels to initiate reactions and even orientation of the molecules during collisions play a role and have to be considered in the application of sonochemistry (i.e. the chemical reaction mechanisms) [8].

Generally, the more collisions, the higher the probability of a reaction taking place. Various parameters affect the collision rate, of which the most common are temperature, pressure, concentration, surface areas and catalysts.

Secondly the energy levels of the reactants need to be high enough to facilitate bond breaking.

Chemical reaction rates are influenced by thermodynamics and kinetics. While thermodynamic data tell us how much energy is gained or released if the reaction takes place, the kinetic factor is more important when considering reaction rates and many factors influence them, including (a) the nature of the reactants, (b) the phase of the reactants, (c) temperature, (d) pressure, (e) concentration, (f) surface area and (g) catalysts.

Kinetics for pyrolysis reactions are often based on the following equations for the reaction rate (r) as a function of concentrations (C) and activation energy (E_a):

$$r = \frac{\delta C_{tar\ compound}}{\delta t} = k(T) \cdot (C_{tar\ compound})^m \cdot (C_{CO2})^n \cdot (C_{H2O})^o \cdot (C_{H2})^p \qquad (1)$$

$$k(T) = k_0 \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \qquad (2)$$

B. *Bubble Dynamics and the Hot Spot Theory*

The creation, oscillation and implosion of bubbles play a vital role in the sonochemical reactor.

The ultrasonic energy is absorbed into the cavitation bubbles thereby inducing the sonochemical reactions. This also corresponds with the observation that the sound absorption coefficient (α) increases dramatically in the sonochemical reactor [5]. The absorption coefficient is therefore a very important parameter in sonochemistry and is affected by the frequency (f), the density (ρ), the speed of sound in the medium (c), the viscosity (η_s), thermal conductivity (k) and the heat capacities (c_p and c_v) of the fluid [6]:

$$\alpha = \frac{2\pi^2 f^2}{\rho c^3}\left[\frac{4\eta_s}{3} + \frac{(C_p/C_v - 1)k}{C_p}\right] \qquad (3)$$

It has been shown that mathematical modelling of bubble dynamics shows good correlation with experimental observation [7].

Dissolved gas in the fluid and/or vaporization of the liquid forms a micro bubble during ultrasonic irradiation. This bubble increases in size as the acoustic pressure decreases. The subsequent compression phase causes the cavity to contract and for specific conditions the cavity collapses in a much shorter time as the expansion phase. Since the collapse time is much shorter than required for mass and heat transfer, the cavity compression leads to high pressure and almost adiabatic temperature rise of its contents.

This explanation of how the extreme pressures (> 100 bar), temperatures (> 5000 K) as well as associated heating and cooling rates (> 10^9 K/s) are caused is referred to as the "hot spot theory". The collapse is followed by an oscillation (the after bounce) until the next rarefaction phase and the start of a new cycle [1].

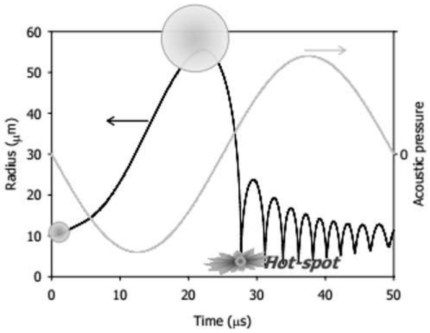

Fig. 1. Cavity formation and collapse [1]

C. *Acoustics*

Sound waves travel through a gas, liquids or solid medium as a longitudinal wave and their characteristics are related by frequency (f), wavelength (γ), speed (ν), bulk modulus of the fluid (K) and the density of the fluid (ρ) as shown in equations (4) and (5).

$$\gamma = \nu/f \qquad (4)$$

$$\nu = \mathrm{sqrt}(K/\rho) \qquad (5)$$

Ultrasonic waves in a closed environment (such as a reactor) reflect from surfaces in the constraining geometry (boundary conditions) and are thus superimposed onto other wave cycles within the system. When the wavelength (or a submultiple thereof) of the acoustic wave corresponds to the distance between two parallel features of the reactor, then standing waves will form. These standing waves appear at very discrete frequencies and have characteristic patterns (also

ISSN: 2521-229X
ISBN: 978-99968-0-608-7

referred to as acoustic modes). Numerous acoustic modes typically exist for any given reactor geometry.

When an ultrasonic excitation frequency coincides with an acoustic mode of a reactor geometry, then that acoustic mode will start to resonate and form a standing wave in the system. The amplitude of the standing wave will depend on the damping in the acoustic system and could in some cases even become destructive to the equipment.

Acoustics are therefore of paramount importance in the field of sonochemistry. Not only will it dictate the locations where sonochemistry will take place, but also what the intensity of the ultrasound will be at those locations. In developing an efficient reactor, it is necessary to carefully consider the acoustic properties thereof.

D. Factors influencing sonochemical reactions

Many efforts have been made by many researchers to enhance ultrasonic irradiation efficiency and the influence of various parameters have been studied.

1) Frequency

The rarefaction phase shortens with increasing frequency and higher power is required to cause cavitation at higher frequencies [2].

On the other hand higher frequencies produce smaller bubbles and higher amounts of radicals. There is also a relationship between resonant frequency and bubble radius and tuning to the appropriate frequency will drive the sonochemical reaction to its maximum yield [9][10].

2) Intensity

A minimum intensity is required to reach the cavitation threshold [2]. The amount of electrical energy which is needed in order to attain the desired ultrasonic intensity depends on many other conditions including the reactor design.

In general sonochemical effects will be increase with an increase in in intensity. While in some cases drastic improvements have been observed with increased intensity [12] it does not necessarily improve the desired outcome [11].

3) Solvents

Bubble collapse produces shear forces in the bulk liquid and viscosity increases the resistance to shear [2].

It has been observed that sonochemical reactions of hydrocarbons are more rapid in polar than non-polar solvents [14].

More volatile solvents support cavitation at lower acoustic energy. Cavitation is difficult in solvents that have low vapour pressure [2].

The vapour pressure has an impact on the yield of radicals during sonochemical reactions [4]. The effective value of polytropic ratio ($\gamma = c_p/c_v$) in the cavitation bubble is a major factor in the radicals yield and in volatile organic solutes the effect of vapour pressure on gamma plays an important role. In aqueous mixtures, different behaviours are observed with organic solvents having vapour pressures higher than water that with organic solvents having vapour pressures lower than water. Therefore organic liquids greatly diminish the intensity of cavitational collapse [3].

4) Dissolved gases

Dissolved gas in the liquid medium has been used to aid in the formation of cavitation bubbles [4]. The energy on collapse increases for gases with large polytropic ratio. Monoatomic gases are preferred [2]. Argon, nitrogen, hydrogen, carbon monoxide and air are some of the common gases used. Saturation of various gases in water enhances the production of the radical H_2O_2 [3]. Polyatomic gases like hydrocarbons reduce the maximum temperatures attained in the bubble since they provide vibrational and rotational modes that will absorb much of the kinetic energy [4][16][17].

5) Surface tension

Liquid-gas interfaces are generated during cavitation. The addition of a surfactant facilitates cavitation [2].

6) Temperature

Higher temperatures cause the vapour pressure to raise and cavitation will be easier. However, this also result in less violent bubble collapse [2].

7) Reactor Pressure

Raising the reactor pressure will produce a larger intensity of cavitational bubble collapse [2].

8) Chemical dosing

The addition of chemicals (e.g. NaCl and $FeCl_3$) has been shown to enhance cavitation in certain cases due to hydrophobic interactions [14].

9) Presence of solid particles

When solid particles exist in the heterogeneous reactant mixture, then bubble collapse becomes asymmetric causing high jets of fluid to shoot into the collapsing bubble space. This jet causes extremely violent fluid dynamic conditions and causes impingement into the solid particle with increased reactivity.

10) Standing waves

Reaction rates depend significantly on the presence of standing waves since cavitation bubbles gather at the anti-nodes of the standing waves by the primary Bjerkes forces [13].

11) Liquid flow

Liquid flow prevents the cavitation bubbles from agglomerating and reaction rates are thereby enhanced. However, little research has been done on sonochemistry under turbulent flow.

III. REACTOR DEVELOPMENT

In order to conducts experiments that are useful, the results need to enable one to scale up later to commercial versions. It is therefore necessary to consider some aspects of large scale implementation as well when designing the experimental reactor.

The selection of ultrasonic parameters such as ultrasonic mode (continuous or pulse), frequency, power, processing temperature, solvent, aeration together with the geometric

ISSN: 2521-229X
ISBN: 978-99968-0-608-7

design of the reactor determines the level and distribution of energy intensity in the system. With these aspects taken into consideration and proper geometric construction it is possible to optimise the efficiency and reliability of the reactor performance [15].

A. *Design considerations*

When designing sonochemical reactors it is important to consider:

- Position of ultrasonic horn in the sonochemical reactor.
- Surface and shape of the tip of the transducer or horn.
- Replacement of a single high-output transducer with an array of transducers having lower power output.
- Superposition of ultrasonic field by changing reactor geometries.

B. *Reactor types*

Various reactor types exist with their own advantages and limitations [15]. In this scenario a reactor type is sought after that easily scalable and has potential to be implemented economically. The following types of reactors are in this category:

1) *Liquid whistle*

Ultrasound is generated by mechanical oscillation. It has the advantages of low cost and is suitable for continuous flow reactions. However, it is limited in frequency and power output.

2) *Probe reactor*

This reactor type delivers ultrasonic energy directly to the liquid reactant through an immersed horn. It has the advantage of high power output and concentrated energy delivery. Although it is already commercialized, its limitations are that the horn tip is easily eroded and that its acoustic intensity distribution is poor. It is also difficult to control the reaction temperature and has low cavitational efficiency.

3) *Resonating tubular reactor*

Ultrasound in this reactor is generated by vibration of resonating stainless steel tubes which contain the reactant which flows through them. It avoids possible contamination of reactants and is capable for handling large-scale feedstock. It has been successful in Phenol oxidation.

4) *Reverberative flow reactor*

Intensified acoustic intensity is achieved by reflection and reverberation techniques. Energy is delivered in concentrated and intensified manner and it produces a uniform ultrasonic field.

5) *Polygonal Reactor Transducer*

An array of transducers surround the polygonal vessel containing liquid reactant. It delivers a concentrated, intensified and uniform ultrasonic field. Due to the polygonal shape of the vessel, it is limited to low reactor pressure applications.

C. *Experimental setup*

The reactor geometry has a great influence on the formation of *standing waves* and small features in the reactor geometry can have a huge impact on the efficiency of achieving this. On the other hand, the structural response of the reactor itself could be used to assist in the creation and amplification of such standing waves (acoustic resonance). In normal circumstances it is good practice to specifically steer away from any such situations since they could easily lead to equipment failure [18]. However, if the system is designed to withstand acoustic induced resonance, huge amounts of energy can be harnessed to assist in sonochemical reactions. It will therefore be one of the aims of this design to create the conditions where fluid-structural interaction is promoted by having acoustic and structural modes coincide. It follows then that it will also be necessary to apply frequency tuning to ensure that the structural and acoustic modes are excited.

The first set of experiments will focus on a batch process in a simple geometry, i.e. a cylindrical vessel. Thereafter the pilot reactor (fig. 2) will be fitted with ultrasonic equipment to study characteristics and performance in a continuous process.

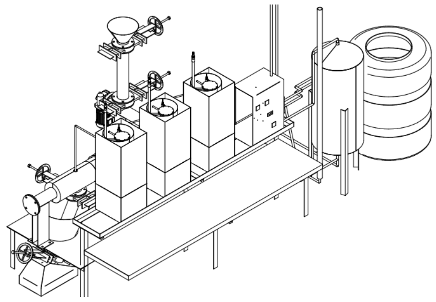

Fig. 2. Pilot Plant at Chemical, Materials and Metallurgical Department

. Both macroscopic and microscopic characteristics in the sonochemical field contribute to the efficiency of the sonochemical reactor. The macroscopic characteristics define what the acoustic field looks like and they are influenced primarily by the geometry of the reactor, but also parameters like fluid density and the frequency and orientation of the ultrasonic excitation source. This acoustic field defines the localised conditions on a microscopic level and together with other conditions e.g. ultrasonic frequency and the physical properties of the fluid, these local conditions affect the local reactions. It is therefore necessary to model on both a macroscopic as well as a microscopic level in order to accurately predict pyrolysis enhancement.

D. *Macroscoping modelling*

The first step in determining the properties of the acoustic field, is to create a 3D model of the reactor. Thereafter, the acoustic modes of the fluid are determined by means of the Finite Element Method (FEM). In addition to determining the acoustic modes, the structural modes will also be determined using the FEM. A study of the acoustic field and structural behaviour will lead to the choice of (a) the location of the

ISSN: 2521-229X
ISBN: 978-99968-0-608-7

ultrasonic transducer and (b) the frequency of the ultrasonic excitation.

E. Microscopic modelling

The hot spot theory will be combined with the principles of bubble dynamics to develop a mathematical model which will aim to predict the localised conditions on a microscopic level. The chemical reactions which take place during pyrolysis will then be added into this model to predict reaction rates. The localised conditions which are determined in the macroscopic analysis will be applied to the microscopic mathematical model.

IV. CONCLUSION

Literature has shown great potential for the promotion of chemical kinetics by the use of ultrasound. However, scalability has always been a challenge and commercial application in the industrial sector is still very limited and it has not yet been applied commercially in the pyrolysis field. This study aims to perform experimental and analytical work where ultrasound is applied to influence pyrolysis reactions and the ultimate goal is to unlock sonochemistry as a commercially viable technique to convert coal and biomass into valuable products.

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