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Petrochemicals: Cellulosic Wastes as an Alternative Source of Feedstock

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1. Introduction

Petroleum, the major feedstock into the petrochemical industry is a depleting natural resource. The rapid growth in world population, coupled with the increasing standard of living means that the petroleum reserves, which although they appear vast (Cheschire & Pavitt, 1978), are still limited and fast running out. Secondly, petroleum is the main source of fuel for the increasing number of automobiles, with the effect that the greenhouse gases generated have already exceeded threshold values. The continuous exploitation of petroleum has led to immense degradation of the environment as is observed in oil spills, and erosion in oil producing areas. There is the need to look for alternative sources of fuel and petrochemical feedstock.

Another problem associated with the increasing world population is the need to grow more food to match the population growth. This need gives rise to increased agricultural activities and food processing which result in the generation and accumulation of large amounts of organic wastes in the form of biomass residues, and consequently, municipal refuse which exacerbates environmental degradation. Appropriate disposal of these wastes is a major problem that requires urgent and long lasting solutions.

Over the years, land filling and incineration have been used to dispose of municipal and agricultural wastes. These methods did not raise any major concerns in the past because of the extremely low rates of waste generation at the time. Today, the large amounts of the greenhouse gases, particularly CO and CO_2 from incineration, and ground water contamination from landfills can no longer be ignored.

These problems are best solved by applying modern waste management techniques. Good management practices aim at reducing the rate of exhaustion of the resource base, rather than increase or even sustain the rate of consumption (Mitchell, 1995). These waste management techniques entail that, waste generation is avoided as much as possible by either reusing waste, combustion to heat energy, and then disposing of the resulting residue by the least environmentally damaging methods.

Studies have shown that the biomass component in waste, predominantly of cellulosic materials, is a heavy energy carrier. For example, Ngomo (2004) estimated that in

Cameroon, 1,148.77 PJ of energy, equivalent to 41,325 million kWh of electricity could be harvested annually from the theoretical harvestable biomass wastes arising from agricultural waste, forest residue, and livestock dung.

As early as 1917, the need to obtain chemicals from cellulosic materials had already been eminent. For example, Palmer & Cloukey (1918) in producing alcohol from various species of hardwoods studied the effect of moisture content in the wood on alcohol yield. By destructively distilling beech, yellow birch and maple that had been subjected to seasoning for between 4 and 18 months they observed that beech gave high alcohol yields when the moisture content was high, while excess moisture lowered the yields for yellow birch and maple.

Palmer (1918) used phosphoric acid to catalyse the destructive distillation of hardwoods. Working at both atmospheric pressure, and at elevated pressures of 412 – 712 kN/m^2, they saw that phosphoric acid increased the yields of alcohol at atmospheric pressure. Hawley (1922) continued the work of Palmer by studying the effect of various chemicals as catalyst. Working at atmospheric conditions, he found phosphoric acid to be unstable; and that promising yields of alcohol were obtained by using sodium carbonate, sodium silicate, and calcium carbonate. In an attempt to produce liquid fuels from cellulose, Fierze-David (1925) arrived at the following results and conclusions: hydrogen had no effect on the dry distillation of wood even under high pressure and that it acted just as an inert gas improving on the mechanism of the reaction; copper hydroxide, iron hydroxide and nickel hydroxide catalysed the distillation of cotton cellulose at 450 - 470^{o}C and 150 – 245 atm. to give a distillate consisting of aldehydes, ketones, phenols, cyclic glycols, and fatty acids.

As reported in Henze et al (1942), Bowen et al (1925) re-iterated the importance of catalyst in the liquefaction of cellulose by concluding that cotton yarn did not undergo any appreciable reduction when treated with hydrogen at 440^{o}C and 12,360 - 13,390 kN/m^2. However, when impregnated with nickel salts, almost the whole material was converted to liquids and gases under the same pressure and temperature conditions. The liquid produced was an opaque viscous tar, containing carboxylic acids, phenols and neutral oils. Frolich et al (1928) also observed that high temperature, high pressure and catalyst were necessary for converting sulphite pulp to liquid and gases. The liquid products consisted of phenols, saturated and unsaturated hydrocarbons.

From all these historical works, and the more recent one by Boocock et al (1980), we can deduce that:

- Cellulosic materials can be converted to a mixture of chemicals consisting of gases, liquids and solids;
- High pressure and high temperature in the presence of catalyst are essential for the conversion and the yield. In addition, the actual liquid yield depends on the extent of pressurizing, heating and the type of catalyst;
- The liquid mixture consists of a variety of substances, which can be used for the production of other chemicals.

Other more recent works applied high temperature and high pressure, but not the use of catalyst, to give the same types of products (El-Saied, 1977; Kaufmann and Weiss, 1975).

Cellulosic materials can be converted to oils and other chemicals by the methods of gasification, pyrolysis, hydrogenation, and hydrolysis and fermentation. Gasification converts the cellulosic materials to syngas (synthetic gas), which is a mixture of CO, H_2, CO_2 and CH_4. The reaction takes place at high temperatures of over 700^{o}C without combustion, and under a controlled amount of oxygen and/or steam. Gasification has the advantages that the syngas produced is a more efficient fuel than the original cellulosic material because it can be combusted at a higher temperature; syngas can be combusted directly in fuel cells and gas engines, and it can be used to produce methanol.

In pyrolysis, the cellulosics undergo an irreversible chemical change caused by heat in the absence of oxygen to give char, organic liquids and water. The reaction is endothermic. The heating value of the pyrolysis products is the sum of the heating value of original cellulosic material and net energy added during the pyrolysis process. In hydrolysis/fermentation, the pre-treated cellulosic material is first hydrolysed to glucose. The product is then converted to a mixture containing alcohols by fermentation, followed by distillation to obtain purer alcohols. The process of hydrogenation converts cellulosic materials to gaseous, liquid and solid products. The cellulosic material suspended in a slurry fluid, and in the presence of hydrogen is subjected to high pressure and heated to obtain the hydrogenation products.

The objectives of this work are to:

- convert cellulosic wastes to chemicals by the process of hydrogenation;
- deduce the mechanism for cellulose hydrogenation;
- deduce a rate expression for the process;
- assess the feasibility of the hydrogenation process by doing an energy economy analysis.

Cellulose, a high molecular weight polymer, with the formula $(C_6H_{10}O_5)_n$ is a structural polysaccharide derived from beta-glucose (Updegraff, 1969). It is the primary structural component in the cell wall of plants and trees. In plants, it is highly imbedded in lignin, which prevents it from being easily accessible.

Cellulose is insoluble in water and in neutral solvents such as gasoline, benzene, alcohol, ether and carbon tetrachloride. It is almost insoluble in dilute acids. In the presence of mineral acids of moderate strength, it degrades into glucose (Cheremisinoff, 1980). Oxygen is removed from cellulose as H_2O and CO_2 in the presence of high reducing agents such as H_2 and CO (Boocock et al, 1979). The close association of cellulose and lignin in plant biomass requires the use of drastic reaction conditions such as pressures above 100 atmospheres and temperatures of 250 – 400^{o}C for their processing (Cheremisinoff and Morresi, 1977).

In batch systems, the reducing agents are generated in-situ by adding a little amount of water. Under the reaction conditions, the cellulose rings are cleaved by the reducing agents. Edewor (1980) represented the liquefaction reaction of cellulose broadly as involving the following steps:

Initiation: this is the shift reaction in which water reacts with a little amount of cellulose to give H_2 and CO_2. This is followed by the generation of free radicals.

In the liquefaction step, the remaining cellulose is cleaved by the free radicals obtained from the H_2 and CO_2 to give a variety of products.

A deduction of the detailed reaction mechanism will be given in the kinetics part below (Section 4).

The major difference between hydrogenation and gasification or pyrolysis is that hydrogenation takes place in a liquid medium. The liquid used is called **slurry fluid**. The slurry fluid is used because, it minimises the charring of the cellulosic materials in favour of its conversion to liquid products. That is, the slurry fluid tends to shift the equilibrium towards the formation of liquid products, thereby reducing the amount of char produced. According to Kaufman and Weiss (1975), a slurry fluid should be thermally stable, have low vapour pressure, and good solvent activity. It should also be cheap and readily available. Water is not a good slurry fluid despite its cheapness and ready availability because it generates excessive steam pressures at high temperatures.

To illustrate the production of bituminous oils from cellulosic wastes, we report the experimentation procedures in the studies of Anagho et al (2004, and 2010) and Edewor (1980).

2. Experimental

2.1 Equipment

- Autoclave: half-litre, high pressure, magnetically-driven, and heated from the exterior by a 1,600 watt heater.
- Infrared spectrophotometer: Model Acculab 10, using NaCl discs.
- Gas chromatograph: Hittachi GC model Carle GC 9700 (Shimadzu, Kyoto, Japan).
- Product separation was obtained using a high temperature hydrocarbon column, Chromosorb G, AW, maintained at 180^{o}C.
- The carrier gas was nitrogen flowing at 40 ml/min, and detection was by flame ionization.

2.2 Chemicals and materials

- The cellulosic materials included leaves, grass, cow dung, and municipal refuse. They were dried and pulverized.
- Gasoil was used as the slurry fluid.
- Hydrogen gas, supplied from a cylinder was used along with water to initiate the reaction.

2.3 Experimental procedure

2.3.1 Liquefaction

Each run used 100 g of slurry fluid, 20 g of dry pulverized cellulosic material, 1.2 g of water sealed into the autoclave, and pressurized to 30 kg/cm^2 by hydrogen. Heating was carried out for 3 hours. During heating, temperature and pressure were recorded over some time

intervals. After cooling down to room temperature, the reactor was opened and the masses of solids (char) and liquid determined by carrying out a material balance on the reactor.

2.3.2 Distillation and analyses of products

The freshly produced hydrogenation product was fractionated into five main fractions as shown in Table 1.

The freshly prepared hydrogenation product (Sample A) and the distillation fractions were analysed using infrared spectroscopy and gas chromatography to determine the types of chemicals generated from the liquefaction.

The Lassaigne's sodium fusion test was also carried out on all the product samples. It is a qualitative test used to show the presence of oxygen, nitrogen, sulphur and halogens in organic molecules. In this test, the element to be identified is first converted into an inorganic ionisable form which can be readily identified by inorganic tests.

In this study, a little quantity of sodium metal was put into a test tube containing a sample of synthetic fuel and heated to red hot to produce the ionisable compounds.

A representative equation for the test is:

$$\begin{pmatrix}\text{Organic compound}\\ \text{containing C, H, N,}\\ \text{O, S, Halogen}\end{pmatrix} + Na \xrightarrow{Heat} \begin{pmatrix}\text{NaCN, NaS,}\\ \text{NaOH, NaHal}\end{pmatrix}$$

The cyanide was analysed using iron (II) sulphate, while the hydroxide was by anhydrous copper sulphate (Anagho et al, 2010).

Sample Label	Sample name	Conditions of Fractionation
A	Freshly prepared sample, before fractionation	
B	1st Fraction of hydrogenation product	Boiling point: 100°C Pressure: 760 mmHg
C	2nd Fraction of hydrogenation product	Boiling point: 200°C Pressure: 760 mmHg
D	3rd Fraction of hydrogenation product	Boiling point: 250°C Pressure: 760 mmHg
E	4th Fraction of hydrogenation product	Boiling point: 300°C Pressure: 760 mmHg
F	Bituminous residue, dissolved in tetralin	

Table 1. Fractionation products from synthetic fuels obtained from cellulose hydrogenation.

3. Results

3.1 Products yield

The masses of the different streams and for the various cellulosic materials are presented in Table 2 below.

Cellulosic material	Solid product (g)	Liquid product (g)	Gaseous product (g)
Leaf	9.00	7.80	3.20
Cow dung	12.00	5.80	2.20
Groundnut husk	10.00	9.80	0.20
Municipal refuse	8.50	9.30	2.20

Average yield: Solid = 49%; Liquid = 40%; Gaseous = 11% (Anagho et al, 2004)

Table 2. Product yield from the hydrogenation of 20 g of cellulosic material.

The table shows that on the average, 40 per cent by mass of the dry cellulose is converted to synthetic oils by hydrogenation. Also, the amount of solid left for disposal is less than 50 per cent by weight of the dry cellulosic material.

3.2 Temperature and pressure evolution during heating

During heating, the temperature rose rapidly from room temperature to about 250^{o}C, and this took about 75 minutes. As heating was continued, the temperature rose slowly to a value of between 300 and 325^{o}C. It then remained constant with further heating.

The pressure in the reactor also increased with time of heating, but in a slightly different manner. Three sections could be identified (Anagho, 2004). The first section corresponded to the first 75 minutes, where there was very little increase in pressure. The increase in pressure may be attributed to pressure–temperature change at constant volume only. This period is regarded as the heat-up time. The second section was the period of rapid rise in pressure and was regarded as the reaction period, and it lasted 100 minutes on the average. The third was asymptotic. The rapid increase in pressure during the reaction period indicates that reaction is by free radical mechanism.

From the reaction time, the reaction rate for each cellulosic material was calculated. The heat-up time, the reaction time and the reaction rate are presented in Table 3 below. The rate of conversion of cellulose was calculated as the ratio of the amount of cellulose converted in gmol cellulose/m^3 solution to the reaction time. (The molar mass of cellulose was taken as 162 g/mol.).

3.3 Analysis of hydrogenation products

IR spectroscopy analyses of the raw cellulose samples showed the presence of the O-H, C-C, C-O and C-N bonds for all the samples. The newly produced substances did not contain O

and N as they lacked the characteristic O-H and C-O bands between 3600 and 3100 cm^{-1} and 1300 and 1000 cm^{-1} respectively. This indicates that hydrogenation removes the oxygen from cellulose.

Cellulosic material	Heat-up time (min)	Reaction time (min)	Reaction rate (mol/m^3s)
Leaf	75.00	100.00	8.57
Cow dung	75.00	100.00	8.57
Groundnut husk	75.00	125.00	6.82
Municipal refuse	100.00	125.00	6.82

Average rate = 7.695 mol/m^3min = 0.128 mol/m^3s. (Anagho et al, 2004)

Table 3. Reaction parameters for cellulose hydrogenation.

The presence of the saturated C=C bond and aromatics as depicted by the IR bands at 1600 and 1400 cm^{-1}, coupled with the GC analysis suggest that many types of compounds, such as aromatics, saturated and unsaturated hydrocarbons, both straight chained and cyclic were produced. When stored under light for some time, sediments formed in the originally homogeneous mixture, while oxygen and nitrogen reappeared to show that the hydrogenation products were unstable (Anagho et al, 2004).

The implication of these observations is that the hydrogenation of cellulose leads to the cleavage of the cellulose ring, followed by the removal of the oxygen in it. Hydrogenation also gives rise to unstable hydrocarbons, which when stored for some time regain oxygen to give saturated and unsaturated oxygenated compounds.

4. Kinetics of cellulose hydrogenation

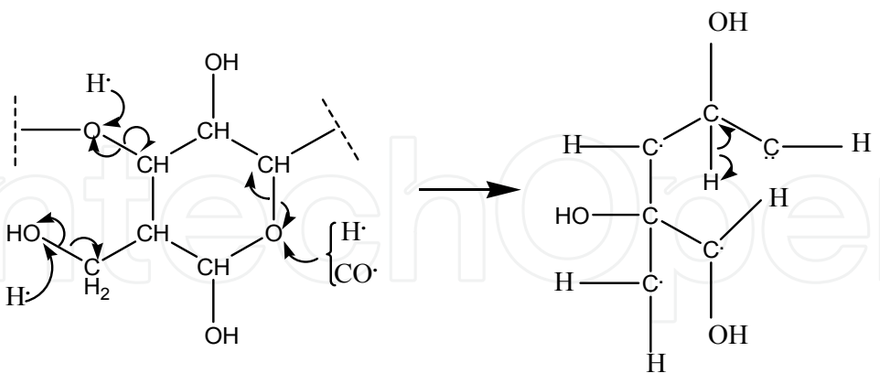
4.1 Mechanism of the hydrogenation process and justification of the products type

As stated above, the cleavage of the cellulose ring during the hydrogenation process leads to the removal of oxygen, followed by the production of a mixture of products consisting of straight chain, branched chain and cyclic hydrocarbon compounds, some of which are saturated and others unsaturated. The process of hydrogenation takes place under high temperature and pressure, and leads to the cleavage of the cellulose ring to give products which are later rearranged to aromatic, naphthenic and unsaturated hydrocarbon compounds. This suggests that cellulose hydrogenation takes place through a free radical mechanism (Anagho, 1987). The cellulose ring is cleaved by the free radicals $CO\cdot$, $O\cdot$ and $H\cdot$ obtained from CO_2 and H_2 generated in-situ from water and cellulose by the water gas shift reaction (Macrae, 1966a). These processes are shown by Equations 1 to 4 as follows:

$$C_6H_{10}O_5 + \tfrac{7}{2}H_2O \rightarrow 6H_2 + 3CO_2 \quad (1)$$

$$CO_2 \rightarrow CO^{\cdot} + O^{\cdot} \quad (2)$$

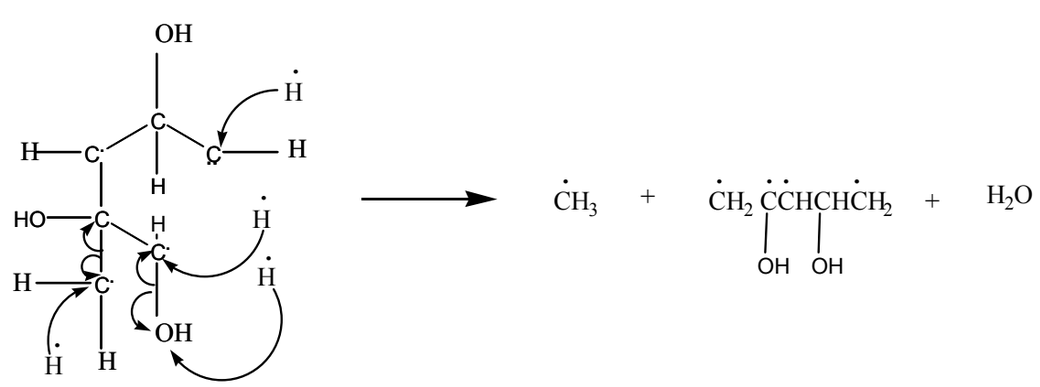
$$H_2 \rightarrow 2H^{\cdot} \tag{3}$$



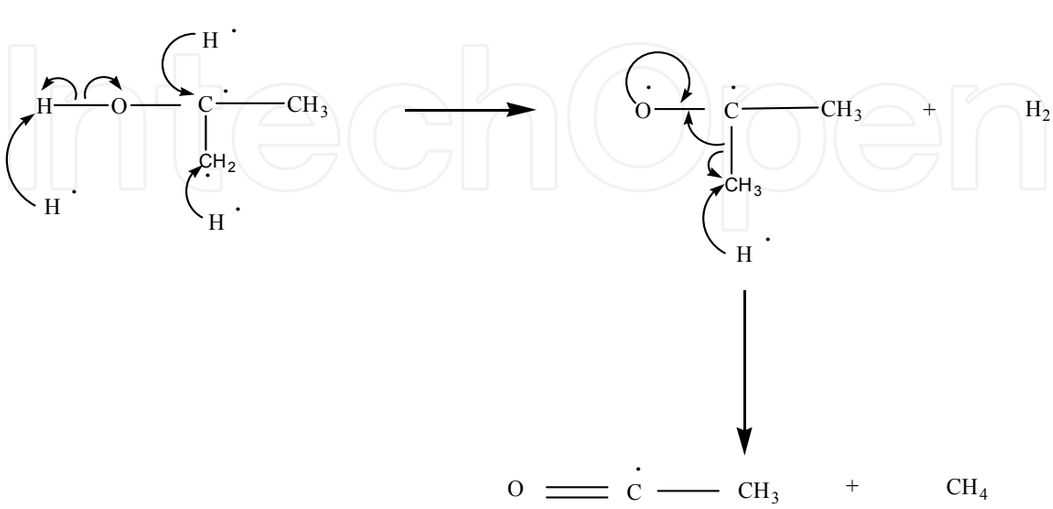
(4)

$$+ \quad H_2O + CO_2 + O_2 + OH^{\cdot}$$

The cleaved ring in Equation (4) further breaks down in various ways into a number of radicals (Equations 5 to 7):

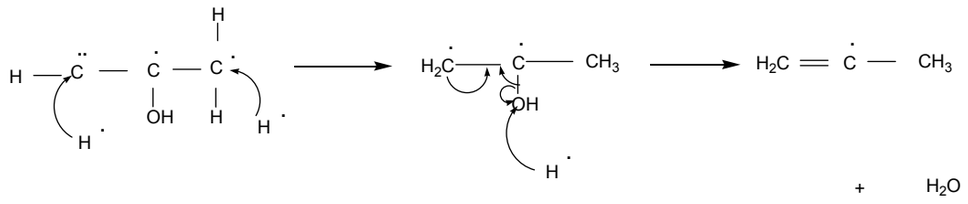


(5)



(6)

And,



(7)

Other radicals likely to have been generated are $\dot{C}_2H_5$, $\dot{C}_3H_7$, $\dot{C}_4H_9$ and $\dot{C}_6H_5$.

During the termination reaction, the radicals recombine in diverse ways to give the many products identified by the infrared and GC analyses. For example, the small sized radicals combine to give H_2, H_2O, CH_4, and C_6H_6 as follows:

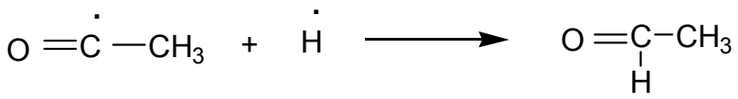
$$\dot{H} + \dot{H} \rightarrow H_2 \tag{8a}$$

$$\dot{H} + OH^{\cdot} \rightarrow H_2O \tag{8b}$$

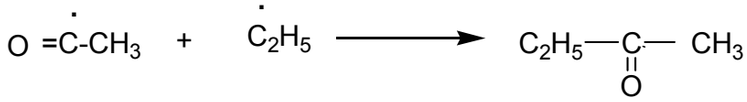
$$\dot{C}H_3 + H^{\cdot} \rightarrow CH_4 \tag{8c}$$

$$\dot{C}_6H_5 + H^{\cdot} \rightarrow C_6H_6 \tag{8d}$$

Aldehydes, ketones and alcohols are also formed as shown by Equations 9 to 11.



(9)

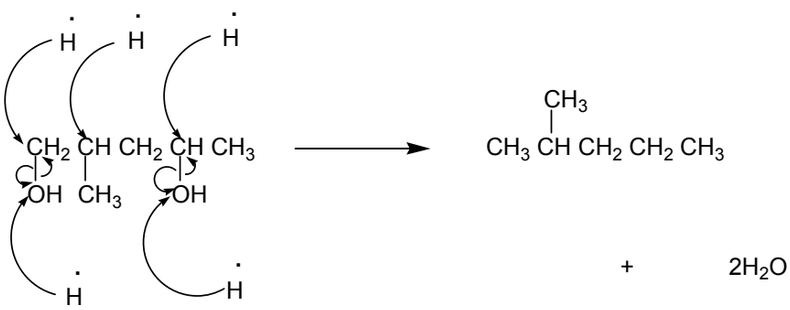


(10)

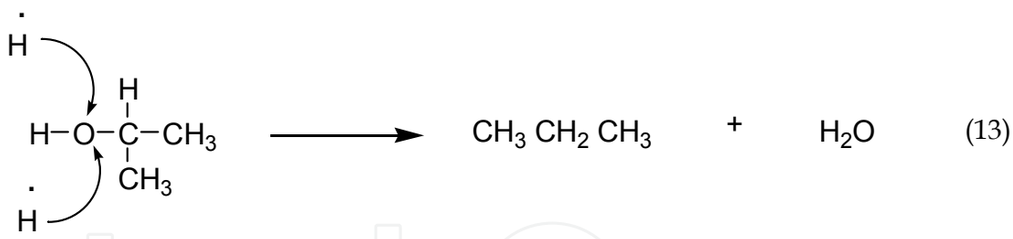


(11)

This is followed by the elimination of the OH group to form aliphatic compounds (Equations 12 and 13).

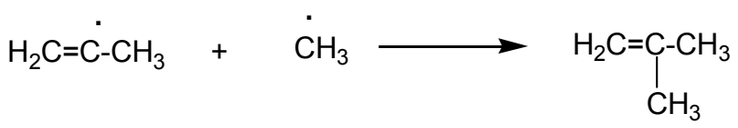


(12)

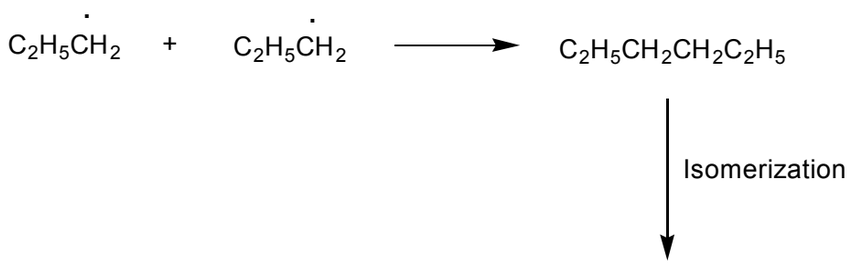


(13)

It is the elimination of the OH group from these oxygenated compounds that explains why the IR analyses on the freshly produced oils show the absence of oxygen. The saturated hydrocarbons, cyclo-hydrocarbons and aromatics can be formed when alkyl radicals combine as shown below in Equations 14, 15 and 16 respectively.



(14)



(15)



(16)

These equations show that the hydrogenation process can be likened to the processes of catalytic cracking and reforming of petroleum in which a variety of saturated, unsaturated, aromatic and naphthenic compounds are produced [Macrae, 1966b].

On storing for some time, the original hydrogenation product (Sample A) and fractions obtained from the atmospheric distillation of Sample A (Samples B to E) were seen to be unstable. They became darker in appearance and sediments were formed at the bottom of their containers. The heavier fractions obtained from the atmospheric distillation of the hydrogenation products exhibited these characteristics the most because it was noticed that the rate of darkening of the products and the formation of sediments appeared faster with the heavier fractions.

IR analyses of these samples led to the following observations:

All samples contained aromatics, with the heavier samples exhibiting more of this characteristic.

The heavier oils and bitumen fractions now contained O-H and C-O bonds to show the presence of oxygenated compounds. These groups were initially absent from the oils when they were just produced, to show that the bituminous oils were unstable and consequently very reactive. They picked up oxygen from the atmosphere during storage. The lighter oil fractions still did not contain oxygen.

The functional groups identified suggest the presence of substances such as benzene, anthracene, phenanthrene, alkenes and other saturated and unsaturated compounds. These compounds are olefins, aromatics and paraffins, which are all essential chemicals, used for the production of many bulk chemicals in the synthesis industry (Macrae, 1966b).

The above observations, that the oils are very reactive and contain substances similar to the essential chemicals used for synthesizing bulk chemicals suggest that the bituminous oils from cellulose or biomass hydrogenation can be used as precursors or feedstock into the petrochemical industries. They can be used as a major substitute or supplement for petroleum whose reserves are continuously being depleted.

The presence of unsaturated and aromatic compounds indicate that the severe reaction conditions for the hydrogenation process [Anagho et al., 2004] led to further breakdown and re-arrangement of the oils produced. This process could be likened to the processes of catalytic cracking and reforming.

4.2 Rate expression for cellulose hydrogenation

As stated earlier, the diverse nature of the products obtained from cellulose hydrogenation coupled with the uncontrollable rise in reactor pressure during the reaction period suggests that cellulose hydrogenation is by free-radical mechanism. In this section we deduce a mechanism for the reaction, from which a rate expression will be obtained. To determine the mechanism, the following assumptions are made:

a. The initiation reaction is the generation of free radicals from CO_2 and H_2 obtained from the in-situ reaction of water and cellulose. The equations for the reactions are equations (2) and (3):

$$CO_2 \rightarrow CO^{\bullet} + O^{\bullet} \tag{2}$$

$$H_2 \rightarrow 2H^{\bullet} \tag{3}$$

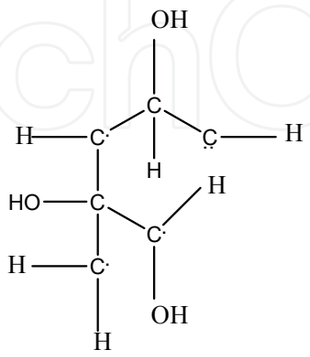
Since the bond energy of the C-O bond in CO_2 is 745 kJ/mol, and that for the H-H bond in H_2 is 436 kJ/mol (Arylward and Findlay, 1974), reaction 3 is considered the only initiation reaction.

b. The cleavage of the cellulose ring can take place at any of the C-C or C-O bonds. Although the C-C bond energy of 348 kJ/mol is lower than 358 kJ/mol for the C-O bond, the cleavage takes place at the C-O bond, because the values are quite comparable in magnitude, and the hydrogen has a higher affinity for oxygen than for

carbon. So if A is taken as a cellulose ring or molecule, and $B^{\bullet}$ the radical after the removal of O, then,

$$A + 2H^{\bullet} \rightarrow B^{\bullet} + H_2O \tag{17}$$

$B^{\bullet}$ can be represented as



c. The cleavage of the cellulose ring is the rate determining step, and our interest is in this step. Therefore, the radical $B^{\bullet}$ does not undergo any further bond breakage into smaller radicals. Instead, the only other propagation reactions are those in which the radical $B^{\bullet}$ sequentially gains $H^{\bullet}$ radicals.

From these assumptions, the following mechanism is deduced.

Initiation:

$$H_2 \xrightarrow{k_o} 2H^{\bullet} \tag{18}$$

Propagation:

$$A + 2H^{\bullet} \xrightarrow{k_1} B^{\bullet} + H_2O \tag{19}$$

$$B^{\bullet} + H^{\bullet} \xrightarrow{k_2} BH^{\bullet} \tag{20}$$

$$BH^{\bullet} + H^{\bullet} \xrightarrow{k_3} BH_2^{\bullet} \tag{21}$$

$$BH_2^{\bullet} + H^{\bullet} \xrightarrow{k_4} BH_3^{\bullet} \tag{22}$$

Termination:

$$BH_3^{\bullet} + H^{\bullet} \xrightarrow{k_5} BH_4 \tag{23}$$

$$BH_2^{\bullet} + BH_2^{\bullet} \xrightarrow{k_6} H_2B - BH_2 \tag{24}$$

$$H^{\bullet} + H^{\bullet} \xrightarrow{k_7} H \tag{25}$$

Using Equation (19), and assuming elementary reaction, the rate of cellulose decomposition is

$$-r_A = k_1[A][H^\bullet]^2 \tag{26}$$

The net rates of consumption of the various radicals are:

$$\begin{aligned} -r_{H^\bullet} &= k_0 P_{H_2} - k_1[A][H^\bullet]^2 - k_2[B^\bullet][H^\bullet] - k_3[BH^\bullet][H^\bullet] \\ &-k_4[BH_2^\bullet][H^\bullet] - k_5[BH_3^\bullet][H^\bullet] - k_7[H^\bullet]^2 \end{aligned} \tag{27}$$

$$-r_{B^\bullet} = k_1[A][H^\bullet]^2 - k_2[B^\bullet][H^\bullet] \tag{28}$$

$$-r_{BH^\bullet} = k_2[B^\bullet][H^\bullet] - k_3[BH^\bullet][H^\bullet] \tag{29}$$

$$-r_{BH_2^\bullet} = k_3[BH^\bullet][H^\bullet] - k_4[BH_2^\bullet][H^\bullet] - k_6[BH_2^\bullet]^2 \tag{30}$$

$$-r_{BH_2^\bullet} = k_4[BH_2^\bullet][H^\bullet] - k_5[BH_3^\bullet][H^\bullet] \tag{31}$$

Applying the steady state approximation that the net rate of consumption of the radicals is zero, and then, expressing all other concentrations in terms of [A] and $[H^\bullet]$, we have that

$$-r_{H^\bullet} = -r_{B^\bullet} = -r_{BH^\bullet} = r_{BH_2^\bullet} - r_{BH_3^\bullet} = 0 \tag{32}$$

And

$$k_2[B^\bullet] = k_1[A][H^\bullet] \tag{33}$$

$$k_3[BH^\bullet] = k_2[B^\bullet] = k_1[A][H^\bullet] \tag{34}$$

$$k_4[BH_2^\bullet] = k_5 BH_3^\bullet] \tag{35}$$

$$k_3[BH^\bullet][H^\bullet] = k_4[BH_2^\bullet][H^\bullet] + k_6[BH_2^\bullet]^2 \tag{36}$$

$$k_5[BH_3^\bullet][H^\bullet] = k_4[BH_2^\bullet][H^\bullet] \tag{37}$$

Since $[H^\bullet]$ is much greater than $[BH_2^\bullet]$, the addition of $H^\bullet$ radicals to $BH_2^\bullet$ radicals occur faster than the addition of $BH_2^\bullet$ radical onto itself. This means that k_6 is negligible before k_4. From this, we have that,

$$k_4[BH_2^\bullet] = k_5[BH_3^\bullet] = k_3[BH^\bullet] = k_1[A][H^\bullet]$$

Substituting for the radicals in Equation (27) when $-r_{H^\bullet} = 0$ gives

$$[H^{\bullet}]^2\{5k_1[A]+k_7\}=k_0P_{H_2}$$

Hence,

$$[H^{\bullet}]^2=\frac{k_0P_{H_2}}{5k_1[A]+k_7} \tag{38}$$

Substituting in Equation (26) gives

$$-r_A=\frac{k_0k_1P_{H_2}[A]}{k_7+5k_1[A]} \tag{39}$$

After the cleavage of the cellulose ring, the termination reaction becomes dominant, and hence, k_1 becomes negligible before k_7; so the denominator of Equation (39) reduces to k_7. Also, hydrogen pressure in the reactor is considered large and hence constant.

Therefore,

$$-r_A=\frac{k_0k_1}{k_7}P_{H_2}[A]$$

And hence,

$$-r_A=k'[A] \tag{40}$$

Where,

$$k'=\frac{k_0k_1}{k_7}P_{H_2}$$

Equation (40) shows that cellulose hydrogenation is first order with respect to cellulose concentration. The reactor pressure increases as the cellulose reacts, to signify that the pressure in the reactor, P is proportional to the concentration of cellulose decomposed.

$$-r_A=kP \tag{41}$$

Equation (41) shows that the rate of cellulose hydrogenation is first order with respect to the total reactor pressure.

5. Economics of cellulose hydrogenation

In the former sections, we established that cellulosic wastes can be upgraded to synthetic fuels by hydrogenation. In this section we will be establishing that such a process is economically feasible. This will be done by carrying out an energy economy analysis. In an energy economy analysis, every cost incurred during a manufacturing process is converted to energy equivalent units.

5.1 Unit cost of production

Benn et al (1980) in an energy economy study considered that the unit cost on the production of synthetic oils was dependent on the three components energy, capital and labour.

$$C = X_f P_f + X_c P_c + X_l P_l \tag{42}$$

Where $X_f P_f$ = energy cost; $X_c P_c$ = capital cost and $X_l P_l$ = labour cost.

In this expression,

C = Total cost per unit of product,
X_f = quantity of fuel (i.e. energy) needed per unit of product obtained,
P_f = price per unit of energy,
X_c = quantity of capital per unit of product,
X_l = quantity of labour per unit of product, and
P_l = price per unit of labour.

In the plant for cellulosic waste hydrogenation, labour cost, $X_l P_l$ includes the cost of transporting the wastes to the plant and the labour in the other aspects in the plant.

$X_f P_f$ is actually the on-site cost of the net energy requirement (NER). NER is part of the gross energy requirement (GER) of the process needed to give the required product less the calorific value (CV) of the product. That is,

$$NER = GER - CV \tag{43}$$

The calorific value is the intrinsic energy of the product from the process. The ratio, NER/CV is the fraction of the product oil (in energy equivalents) that is used up during the conversion process. That is,

$$\frac{NER}{CV} = X_f \tag{44}$$

Hence, the net energy fraction recoverable from the process is $1 - X_f$.

As a first approximation, the cost of fuel for the process is equal to the total cost of producing the synthetic fuel. This is because more than 85% of the required fuel for the plant is generated locally. That is, $C \approx P_f$

Hence,

$$P_f = X_f P_f + X_c P_c + X_l P_l$$

$$\therefore C = P_f = \frac{X_c P_c + X_l P_l}{1 - X_f} \tag{45}$$

The equation shows that the cost per unit of product is the ratio of the nonfuel costs to the net energy yield. The equation also shows that no fuel is brought in from out of the plant, and that fuel inputs can be costed at the on-site value.

The values of X_f and C are determined from the energy equivalents of equipment and inputs into the plant. These components include capital equipment, electricity, chemicals, furnace, boiler and hydrogen plants, organic wastes and waste collection.

When the cost of a plant of a given capacity is known, then the cost of another of a different capacity can be found by using the seven-tenths rule given as:

$$\frac{Cost_2}{Cost_1} = \left(\frac{Capacity_2}{Capacity_1} \right)^{0.7} \tag{46}$$

The subscript, 1 stands for the reference plant, while subscript 2 stands for the new plant.

5.2 Energy requirements of plant and inputs

In the manufacture of the components of the capital equipment and chemicals, many processes are involved, each of which requires an energy input. The cost of the component depends on the total energy cost incurred during its manufacture. Edewor (1979) reported that Casper et al carried out an evaluation of the ratio of the input energy to the pound sterling for a number of products from manufacturing processes. This ratio is called the energy intensity of the product, and it is a measure of the cost of the equipment. They gave the energy intensity of heavy engineering products as 106.28 MJ/£ (1968), and for chemicals as 339.13 MJ/£ (1968). These figures are upgraded to 2011 costs by using cost indices as follows:

Energy intensity (MJ/£ (2011)) = [Energy intensity (MJ/£ (1968)] x

[Cost index (1968)/Cost index (2011)] (47)

The energy equivalent, also called the energy requirement of any capital equipment is then obtained by multiplying the energy intensity by the cost.

The energy equivalents or energy requirements for the components of a 1000 tonne per day plant for cellulose hydrogenation are presented in the table below.

Plant Component	**Energy requirements (x 10^3 MJ/day)**
Capital equipment	295
Electricity	1,429
Chemicals	348
Furnace, boiler and H_2 plants	6,443
Organic wastes	22,107
Waste collection	53
Total = GER (Gross energy requirement)	30,675

Table 4. Energy requirements for the components of a 1000 tonne per day cellulosic waste hydrogenation plant.

5.3 Process energy factor and thermal efficiencies

Although the main objective in the hydrogenation of cellulose is to produce oil products, three product streams are obtained: oils, gases and char. The gas yield is only 15% of the cellulose fed, while that of char is significant. The gases produced are consumed completely in the plant. This means that the process produces only oil and char. Hence, the GER into the process is shared between oils and char. If D is the fraction of the GER that goes to produce oils only, then,

D = (Energy output from process through oil)/ (Total process energy output)

That is,

$$D = \frac{M_o(CV_o)}{M_o(CV_o) + M_c(CV_c)} \tag{47}$$

Where, M_o and M_c are the masses of oils and char respectively, while CV_o and CV_c are their calorific values.

For a unit mass of oil produced,

$$NER = \frac{(GER).D}{M_o} - CV_o \tag{48}$$

The process energy factor is

$$X_f = \frac{NER}{CV_o} \tag{49}$$

X_f is a very significant quantity in the energy economy analyses. It is a measure of the ratio of the total energy demand for the process to the total energy yield from it.

For $X_f \geq 0.6$, the process is considered to be energy demanding, and hence, heavily dependent on energy. It is therefore an expensive process, and may not be economically feasible. Conversely, for $X_f \leq 0.4$, the process is energy rewarding, and consequently, inexpensive.

The thermal efficiency of the process with respect to the oils is defined as the ratio of the energy output of the process through the oil product to the gross energy requirement.

$$\eta_{oil} = \frac{M_o(CV_o)}{GER} \tag{50}$$

By considering the char also, the efficiency becomes

$$\eta_{oil+char} = \frac{M_o(CV_o) + M_c(CV_c)}{GER} \tag{51}$$

Table 5 gives the values of GER, NER, X_f, and thermal efficiencies for the 1000 tonne per day cellulose hydrogenation plant. The plant was designed by Anagho (1987) for the treatment

of municipal waste in Lagos. The design was based on the Kaufmann and Weiss (1975) 36 tonne per day plant that was used to recycle municipal waste in Manchester, UK.

Property	**Magnitude**
GER (x 10^3 MJ/tonne)	53.95
NER (x 10^3 MJ/tonne)	16.30
X_f	0.439
1 – X_f = recoverable fraction	0.561
Thermal efficiency with respect to oils, η_{oil}	35.30%
Thermal efficiency with respect to oil and char, $\eta_{(oil+char)}$	69.50%

Table 5. Energy requirement, energy factor and thermal efficiency for 1000 tonne per day cellulose hydrogenation plant.

The energy factor for the plant is X_f = 0.439. Although this value is smaller than 0.60, it is slightly greater than the maximum value for the plant to be economically feasible, it could still be considered as such. The value will get smaller, and the process more competitive when the present petroleum prices get higher.

6. Conclusions

Cellulose hydrogenation is a complex process in that it takes place under very drastic conditions of high temperature and high pressure, producing a mixture of chemical products. This study shows that the complex reaction can be modelled as a first order rate process with respect to the total reactor pressure. That is,

$$-r_A = kP \tag{41}$$

The hydrogenation generates liquid products at a yield of almost 35% by the mass of the dry pulverised cellulose feed. The products obtained are a mixture of saturated, unsaturated paraffinic and aromatic hydrocarbons, which exhibit instability on storage. An energy economic evaluation of a prototype cellulose hydrogenation process shows that it is an economically feasible process.

The high yield of liquid products, the reactivity of the liquid products and the feasibility of the hydrogenation process suggest that we now have a bioresource substitute for petroleum.

Unfortunately, the technology for obtaining chemicals from cellulose is not well developed. Consequently, it is not widely used to meet the objectives of supplementing petroleum and reducing environmental pollution. The feed into the process comes from so diversified sources of cellulose that the design of plants to process them is difficult.

Future research will look at obtaining alcohols as the main chemicals from bioresource and then using them as the feedstock into petrochemical industries. This will be done by

thermally breaking down the lignin surrounding the cellulose, followed by hydrolysing and fermenting the resulting sugars into alcohol. This will call for research into the growing of fast growing crops that have no particular food values to human beings. In addition to being fast growing, these crops should not compete for agricultural lands.

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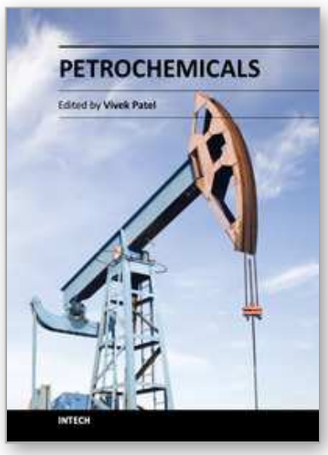
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