PRODUCTION OF ACTIVATED CARBON FROM SOUTH AFRICAN SUGARCANE BAGASSE

By

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ABSTRACT

South Africa has an annual sugarcane milling capacity of about 22 million tonnes on average producing about 3.3 million tonnes of dry bagasse, of which one third is surplus to factory requirements. Currently surplus bagasse is used for furfural, pulp and paper and cogeneration but significant amounts still remain. This prompted the need to find viable alternative and appropriate technology to utilize the surplus.

A laboratory pilot plant was used to investigate the production of activated carbon from bagasse. Experiments were carried out to investigate conditions for making the best activated carbon in a rotary batch kiln, and also to examine potential energy recovery from process gases using Gas Chromatography. Derived results from the laboratory experiments were used to develop a conceptual design for a demonstration plant sited within a sugar mill. The conceptual design was evaluated for economic and environmental impacts using a robust Excel spreadsheet and GABI-3 modelling software respectively.

Excellent activated carbon was produced from sugarcane bagasse by a two-stage physical process involving pyrolysis and gasification with steam. The best operating conditions were pyrolysis at 700°C for 1 hr and activation at 850°C for 1hr, a heating rate of 10°C/min and a steam flow of 15g/g of char per hour. The active carbon yield was 7% on dry bagasse basis with a Methylene Blue Number of 257mg/g of carbon. The active carbon had a sugar decolourisation capacity of 20% at a carbon dosage rate of 0.7 wt% on Brix using clear juice (12°Brix) and 70% at 0.5 wt% on Brix using brown liquor (65°Brix). The Freundlich isotherm showed that the bagasse-based activated carbon was a suitable adsorbent for sugar colour bodies.

Gas analysis results revealed that the off gases from the pyrolysis and activation stages had calorific values of about 63MJ and 31MJ per kg of activated carbon respectively. The total combustion energy of 94 MJ/kg of active carbon was enough to satisfy the process energy requirements for drying, pyrolysis and activation. By burning combustibles like tar, methane, carbon monoxide, ethylene and hydrogen for process thermal energy needs, the environmental impact of the manufacturing process was reduced to a Global Warming Potential of 11kg CO_2 Equiv per kg of carbon produced.

The demonstration plant requires a capital investment of US$10.4 million to give a competitive bagasse-based activated carbon (BPAC) selling price of US$1.80 per kg and IRR, ROI and Investment payback time of 17.93%, 23.93% and 3.80 years respectively. A sensitivity analysis was also carried out to investigate the effect of possible variation in the main project forecasts which are BPAC selling price, bagasse buying price, capital investment and production costs on IRR, ROI and payback time. The benefits of process integration within a sugar mill would be expected to improve the business feasibility; If bagasse was free the IRR would increase to 28.59% and even better to 32.12% if extra boiler and electricity capacity was also available at the mill.

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NOMENCLATURE

Symbol	Description
b	Langmuir constant
C_e	equilibrium concentration of colour in solution, ICUMSA units
C_b	colour of blank, ICUMSA units
C_s	colour of solution, ICUMSA units
D	diameter, mm
d_p	particle size diameter, microns
F	final sample methylene blue concentration (mg/l) from graph x dilution
I	initial methylene blue concentration, mg/l
id	internal tube diameter, mm
K_a	Freundlich constant
m_n	mass of nitrogen gas, g
m_s	mass of steam, g
m_n	mass of nitrogen, g
M_c	mass of carbon, g
M_i	molecular mass of component i, g
M_n	molecular mass of nitrogen gas, g
M_s	molecular mass of steam, g
n	number of moles, moles
n_c	Freundlich constant
od	outside tube diameter, mm
ρ_s	density of steam, kg/m^3
ρ_n	density of nitrogen, kg/m^3
P	pressure, kPa
P_i	partial pressure of component i, kPa
P_n	partial pressure of nitrogen, kPa
P_s	partial pressure of steam, kPa
Q	monolayer adsorption capacity, ICUMSA units/g
q_e	amount of colour adsorbed per unit weight of carbon (ICUMSA units/g)
R	gas constant, 8.314 J/mol.k
S_{BET}	BET surface area of the adsorbent, m^2/g
T	temperature, K
tch	tonnes of cane per hour
v_s	volumetric flowrate, ml/min
v_n	volumateric flowrate, ml/min

V	ideal gas volume, m^3
V_s	volume of contacting stock solution, cm^3
wt %.	weight as a percentage
w_{aa}	weight after activation, g
w_{rm}	weight of raw material, g
w_{ap}	weight after pyrolysis, g
X	amount of colour adsorbed at equilibrium, g-Equiv colour units

Abbreviation	**Definition**
ADP	Alkaline Degradation Products
BET	Brunauer – Emmet – Teller
BPAC	Bagasse – based Powdered Activated carbon
EIA	Environmental Impact Assessment
GAC	Granular Activated Carbon
GC	Gas Chromatography
GCV	Gross Calorific value, kJ/kg
GSV	Gas Sampling Valve
HFC	High fructose Corn syrup
ICUMSA	International Commission for Uniform Methods of Sugar Analysis
IUPAC	International Union of Pure and Applied Chemistry
MS 5A	Molecular Sieve 5A
NCV	Nett Calorific Value, kJ/kg
PAC	Powdered Activated Carbon
PC	Personal Computer
ROI	Return On Investment
SASA	South African Sugar Association
SHE	Safety, Health and Environment
SMRI	Sugar Milling Research Institute
t.c	tonnes of cane
TCD	Thermal Conductivity Detector
TGA	Thermogravimetric Analyser
UKZN	University of KwaZulu-Natal

INTRODUCTION

Background of the project.

The sugar industry of South Africa faces difficult times partly attributed to low sugar prices, the strong rand, and introduction of HFCs and other non-caloric alternatives and hence the need to look for new perspectives and diversification options in order to improve business viability. Unlike sugar production which uses proven technologies, diversification faces many challenges, especially the development of new technology for re-utilisation of by-products and wastes. These technological alternatives have to be assessed separately and within each country concerned because of the unique conditions determining their viability. Currently South Africa has a growing economy with an annual inflation less than 5% and therefore provides a healthy economy for businesses to embark on new projects that involve capital expenditure.

The importance of bagasse as a low cost, renewable, abundant and environmentally clean (act as a carbon sink) by-product of sugar milling is known. Historically, the primary use for bagasse generated in the sugar process was generation of steam by the mills for their energy requirements. However improved steam economy and boiler efficiencies in many factories resulted in surplus bagasse. Surplus bagasse was traditionally left on site, burned or allowed to rot. Current commercial uses of bagasse include manufacture of paper and board, cattle feed and furfural production but some mills are still generating a surplus. The renewed interest to utilize surplus bagasse for making activated carbon comes in the wake of deforestation and depleting reserves of fossil fuels, negative effects of the latter to the environment in terms of global warming and generation of acid rain, and the search for technologically viable alternative processes. Apart from better environmental impacts, industrial 'ecology' offers multiple advantages such as generation of new projects, energy self-sufficiency and increase in the overall economy of the process

The disposal of surplus bagasse has become a problem in sugar factories over the world that are yet to diversify into other projects such as cogeneration, paper and furfural production. Some factories have resorted to landfills and incineration as disposal methods. Bagasse landfills pose a potential hazard due to the risk of spontaneous combustion as a result of microbial activity in the dumps. However there are many opportunities that are available that will reduce the volumes of surplus bagasse. The production of activated carbon is one attractive alternative that offers huge opportunities to overcome these problems and to generate additional income for the sugar mills. Alternatively the activated carbon could be used by the mills themselves to decolourise sugar and provide an additional decolourising agent for sugar thereby improving the competitiveness of local sugar on the world market. Currently there is no industrial application of the production of activated carbon from bagasse anywhere in the world. The closest commercial application of bagasse to activated carbon production is the production of cane coal – charcoal briquettes at Chemelli sugar factory in Kenya. However the commercial production processes and conditions used to produce activated carbon from other precursors are kept under 'lock and key' necessitating the need for research into the production of the same from bagasse

Activated carbon is a versatile product and its importance is based on its high adsorptive capability and amphoteric properties which enable the adsorption of cationic and anionic adsorbates. The important characteristics of activated carbon for both liquid and gas adsorption applications are their high surface area of up to 1500m^2/g, well developed porous structure and surface chemistry. The high surface area is predominantly pores less than 2nm (micropores) and larger pores in the range 2 – 50nm (mesopores) are important in the adsorption of larger molecules like colourants. Pore diameters above 50nm (macropores) do not contribute significantly to the adsorption process and serve as passageways for adsorbates to access meso- and micropores. These characteristics are the reason why activated carbon is currently used in a wide spectrum of industry. According to Bansal (1988), activated carbon is used to purify, decolourise, deodorize, dechlorinate, detoxicate, filter, recover salts and as catalyst and catalyst supports. A summary of the uses of activated carbon in South Africa is given below. Activated carbon is generally an expensive option in the absence of suitable and inexpensive regeneration procedures for the adsorbent (Valix et al 2004), hence the need to exploit bagasse by using appropriate technology to make low cost carbons.

Estimates of the activated carbon market in South Africa (Gore, 1988)

Industry	Usage, Tonnes per annum
Gold recovery	6300
Decolourising	700
Potable water	150
Sasol water purification	Not available
Pharmaceutical	200
Wine and Fruit juice	100
Bottling companies	50
Waste water treatment	Not available
Total Imports (estimate)	9000

Objectives of the project

The initial objectives of this study were to:

- Convert a batch laboratory process producing activated carbon from bagasse to a continuous pilot scale plant.
- Establish the financial implications of the manufacturing process
- Consider all environmental aspects
- Make design recommendations for a demonstration plant

These objectives were reviewed after considering the time and resources available and the final objectives were to:

- Establish conditions for BPAC production in a pilot scale plant – rotary batch kiln
- Establish potential energy recovery from process off gases
- Establish the financial implications of the manufacturing process
- Consider all environmental aspects
- Make design recommendations for a demonstration plant

Research Methodology

The present study was focused on the development of a sustainable process for the production of activated carbon from diffuser bagasse by a two-stage physical. Initial studies on the feasibility of the two-stage activated carbon process were carried out by Devnarain (2003). The process consisted of pyrolysis of bagasse to produce char and subsequent activation of the char by partial gasification with steam. Pyrolysis is defined as the thermal degradation of biomass in the absence of air or in an inert environment and activation is the process of enlarging the surface area available for adsorption in the carbon.

The active carbon production process was carried out under a variety of conditions to investigate scale up effects and optimize the process to get suitable conditions for a demonstration plant. The best activated carbon from the process was compared to commercial products on the basis of adsorption capacity and the kinetics of colour removal from sugar solutions.

The final conceptual design was investigated to evaluate its economic and environmental impact. GaBi-3 Modelling software was used to evaluate the environmental impacts using a Life Cycle Assessment method. Minimisation of energy consumption was an important aspect to the success of the project and the conceptual design was evaluated under a variety of options by which the process would lose the least amount of energy while performing the desired process functions. These options significantly minimized environmental aspects and improve the economics of the overall business. Since the process is energy intensive, it was expected that the price of the final product would be directly depended on the cost of energy for the process.

BAGASSE CHARACTERISTICS AND USES

2.1. Bagasse

Bagasse is the fibrous solid waste generated during the production of sugar from sugar cane. Rasul *et al* (1999) describes bagasse as the crushed remnants of sugar cane stalks after extraction of juice, consisting of three main components namely pith, fibre and rind mixed in different proportions. Typical bagasse consists of about 70% short fibres and 30% long fibres on dry mass basis. There are two methods of extracting juice from sugarcane, the diffusion process and the milling tandem and each method generates a different kind of bagasse. In South Africa about 3.3 million tonnes (dry basis) of bagasse are produced yearly by the 14 sugar factories located mainly along the KwaZulu-Natal coast. The total annual cane production is shown in Appendix G.

2.2. Diffusion process

Sugarcane is weighed and fed to the cane preparation section where it is cut into smaller pieces by cane knives and shredders (see Figure 2-1) The final mass of shredded cane is conveyed into a solid-liquid extractor (diffuser). The perforated floor of the diffuser is furnished with a chain conveyor which carries the shredded cane in counter-current to the hot water flow. In the diffuser, sugar is extracted from the disintegrated cane cells using hot water at about 75 - 80°C. The primary juice produced from the diffuser is filtered via DSM screens before being taken for further processing. The product from the diffuser is de-watered and squeezed using miller rollers to release residual sugar, and the final bagasse has a moisture content of about 50 mass%. Most of the final bagasse is sent to the boilers for steam production.

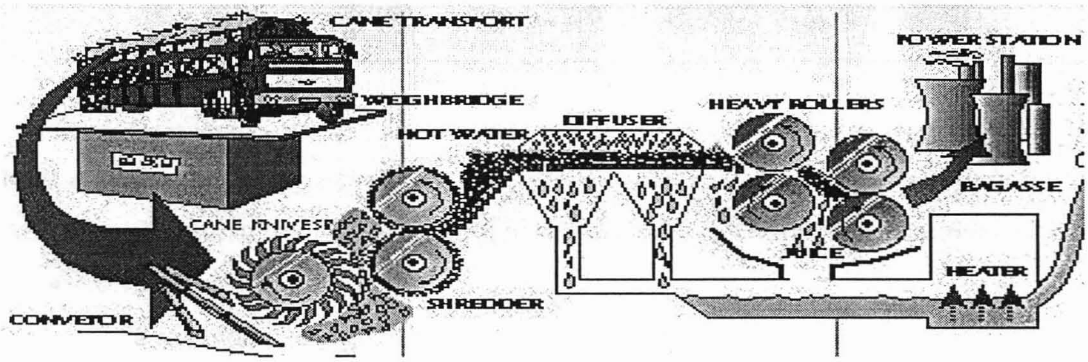

Figure 2-1Diffusion process (courtesy of SASA)

2.3. Mill tandem process

Cane goes through a communition stage before being fed to a series of crushing roller mills to squeeze out the sugar juice. A milling tandem usually consists of four to six sets of roller mills in series. Fibre tend to trap residual juice, and to reduce the amount of sugar lost with the final bagasse, hot water is used to dilute this juice towards the end of the tandem. The juice produced is taken for further processing to produce sugar while final bagasse is conveyed to the boilers for steam production.

2.4. Properties of bagasse

The actual composition of bagasse depends on the following factors:

- Sugar cane variety
- Soil conditions and agronomic techniques
- Climatic conditions especially during harvesting
- Residual foliage, tops and roots in harvested cane
- Green cane or pre-burn harvested cane
- Duration between burning and processing
- Specific processing conditions during extraction processes, mainly temperature, pH value and extraction time and
- Degree of cane preparation.

Typical chemical and physical properties of bagasse are given in Table 2-1 below.

Table 2-1 Analysis of typical sugarcane bagasse (Paturau, 1969)

Typical composition, wt%		Proximate Analysis, wt%		Ultimate Analysis, wt%	
Moisture	49	Fixed carbon	7.0	Carbon	23.7
Fibre	48.7	Volatiles	42.5	Hydrogen	3.0
Solubles	2.3	Moisture	49	Oxygen	22.8
		Ash	1.5	Moisture	49.0
				ash	1.5

The calorific value of bagasse is the amount of heat which is released by the combustion of a unit mass. On average, the calorific value of dry bagasse can be taken as GCV = 9828 kJ/kg and NCV = 8060 kJ/kg (Hugot, 1986).

According to Paturau (1969) one ton of mill run bagasse (49% moisture) is equivalent to:

- 0.18 ton of fuel oil
- 0.28 ton bituminous coal
- 0.15 ton natural gas
- 0.55 ton wood (air dried)

An investigation by Devnarain (2003) showed that ash can be as high as 5.98% of the bagasse (from Sezela Mill) on a dry mass basis compared to 3% by Paturau (1969). However the properties of bagasse can vary widely depending on a number of factors as discussed above. The importance of ash is discussed in detail in Section 5.1. The major component was silica with silicon making up to 45% of the ash. The results of the investigation are summarized in Table 2-2.

Table 2-2 Concentration of ash components in sugarcane bagasse (Devnarain, 2003)

Component	Dry mass% bagasse	Dry mass% ash
Aluminum	1.47	24.58
Silicon	2.67	44.65
Phosphorus	0.75	12.54
Sulphur	0.07	1.17
Potassium	0.04	0.67
Calcium	0.58	9.70
Iron	0.40	6.69
Total	5.98	100

2.5. Comparison of bagasse and with other biomass

The results in Table 2-3 show that bagasse has relatively higher cellulose and lower lignin compared to coconut shells. Coconut shells are already being used for activated carbon production on a commercial basis because of their high lignin content, low ash and their high abrasive resistance among other factors.

Table 2-3 Composition of Bagasse compared to other biomass species (Zanzi, 2001)

Species	Cellulose	Hemi-cellulose	Lignin	Extractives	Ash
Bagasse 2	41.3	22.6	18.3	13.7	2.9
Coconut shell 2	36.3	25.1	28.7	8.3	0.7
Corn stalks 2	42.7	23.6	17.5	9.8	6.8
Olive husk 1	24.0	23.6	48.4	n.a.	4.0
Wheat straw 2	30.5	28.9	16.4	2.4	11.2-6.6
Rice husk 2	31.3	24.3	14.3	8.4	23.5
Rice straw 2	37.0	22.7	2.6	2.1	19.8-16.1

1 wt % dry and extractive free basis, 2 wt % dry basis, n.a.: not analysed

Table 2-4 shows a comparison of physical and chemical properties between bagasse and wood. The results show that quality of bagasse as a precursor for production of activated carbon can be improved to match those of hardwood by removing the pith fraction. The results are summarized below.

Table 2-4 Comparative characteristics of wood and bagasse (Chen and Chou, 1993)

	Wood		Bagasse		
Characteristic	**hardwood**	**softwood**	**whole**	**fibre**	**pith**
α-cellulose (%)	38 – 48	40 – 45	30 – 39	38 – 43	26 – 36
Pentosans (%)	20 – 25	10 – 13	24 – 30	27 – 32	28 – 33
Lignin (%)	20 – 29	26 – 34	18 – 22	20 – 23	18 – 22
Ash (%)	0.3 – 1.2	0.2 – 0.8	1 – 4	0.6 – 1.2	1.8 – 4.6
Ave. length of fibre (mm)	0.7 – 1.6	207 – 3.6	-	1.0 – 2.0	0.25 – 0.4
Ave. diameter (μm)	20 – 40	32 – 43	-	14 – 28	54 – 87
*Ave. density (kg/m^3)	550 – 800**	400 - 500**	-	550*	220*

* Garcia-Perez *et al* (2002) ** Bansal (1988)

Garcia-Perez *et al* 2002 reports that bagasse sifting in a Hoskin Scientific sifting machine revealed that ash content was highest in smallest particles and additionally the finest particles exhibited a very low bulk density (220kgm^{-3}) in comparison to the larger particles (550kgm^{-3}).

2.6. Current uses of bagasse in South Africa

It's difficult to give a general figure as to how much surplus bagasse could be generated by a factory because this depends on the type of equipment installed at the factory and whether there is a backend refinery. Also surplus bagasse is rarely weighed at the factory and unless baled, weight of loose bagasse is often unreliable. Surplus bagasse can be generated by improving steam economy and Felixton Mill is reported to have capacity to produce 45% surplus bagasse (Reid and Rein, 1983). According to Paturau (1969) a modern factory, electrified, operating with medium to high pressure steam and a quintuple evaporator station will require about 425 to 450 kg steam/t of cane which gives a fibres in cane of 9 to 10 mass% by thermal balance. Most South African sugarcane varieties have fibres greater than 15 mass% which indicates a difference in fibre percent of 5 to 6 mass%. This indicates that up to 40% of total bagasse should be available at a similar factory as surplus. Getting rid of surplus bagasse by incineration (by reducing boiler efficiency) is a relatively cheap method of disposing the surplus waste but the process generates fly ash some of which is entrained with the gases in the stacks causing air pollution unless gas cleaning equipment is installed, which can be costly because of the volumes. Despite this practice, Valix *et al* (2004) reports that surplus bagasse is still generated. Other uses of bagasse are listed in Figure 2-2.

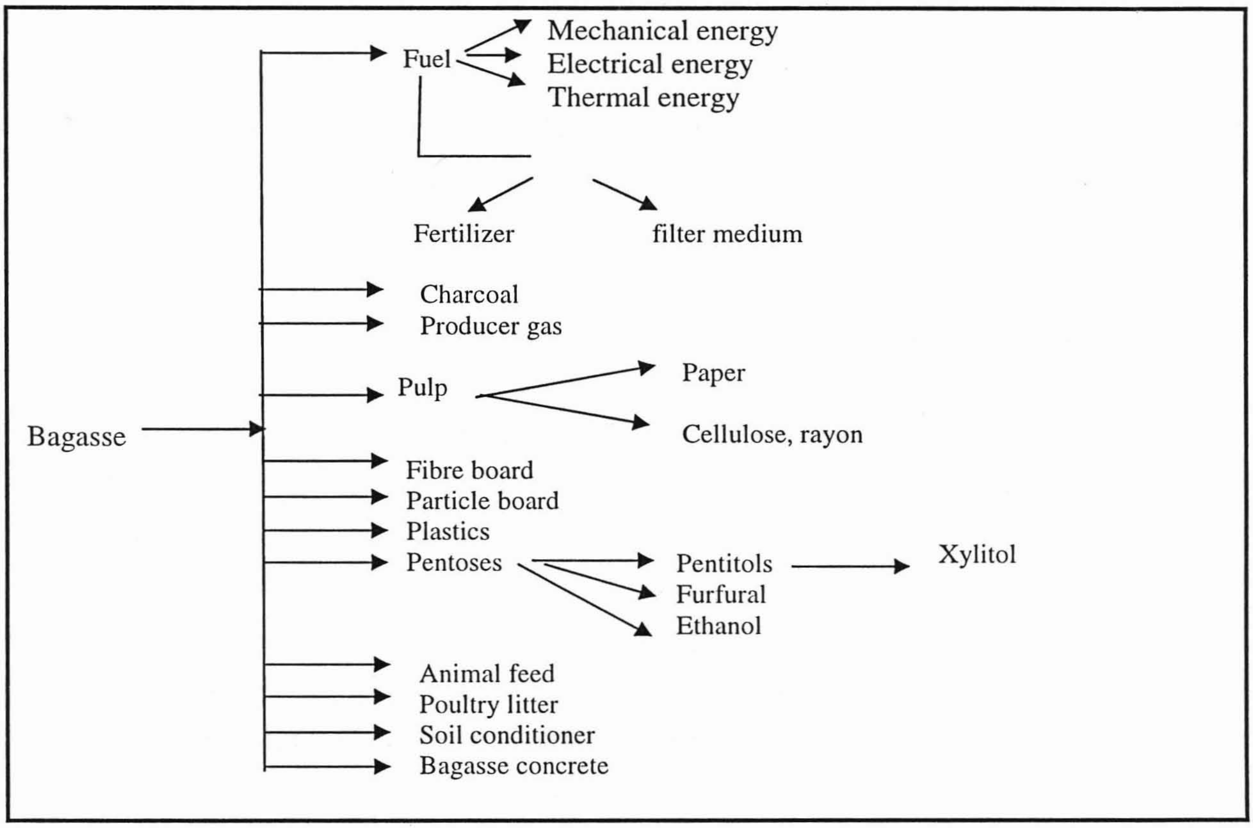

Figure 2-2 A summary of bagasse uses (Van der Poel *et al* 1998)

2.7. Bagasse as a raw material for activated carbon

Bagasse has a low heat of combustion compared to other fuels (Section 2.4) and its extensive use as a primary fuel may be considered as wasteful (from an energy point of view) though its use maybe justified upon economic and practical considerations (Drummonds, 1996). Garcia-Perez *et al* (2002) reported that power generation by direct combustion of bagasse in boilers has a maximum efficiency of 26%. Bagasse transformation into high density renewable fuels like charcoal and bio-oil or chemicals like activated carbon could offer significant economic advantages to sugar mills. Hence the drive to continuously look for other alternative industrial uses. Whilst other avenues for industrial use of bagasse have been realized elsewhere, production of activated carbon from bagasse by a two stage process (carbonization followed by steam activation) remains theoretical rather than practical (Zandersons *et al* 1999). The closest attempt to industrial application is a study by Ng *et al* (2002) on process design and economic evaluation of the manufacture of bagasse-based granular activated carbon. Most of the practical oriented publications deal with chemically activated carbons. However chemical activation is associated with problems some of which are discussed in Sections 4.4.1.

Advantages of bagasse over other activated carbon precursors include:

- Bagasse promises to be one of the several agricultural residues for activated carbon production because it is renewable, safe and in copious supply. This view is also supported by Castro *et al* (2000) who reported bagasse as a very attractive alternative waste for active carbon production.
- Studies by Pendyal *et al* (1999), Ahmedna *et al* (2000) and Marshall *et al* (2000) showed that bagasse-based activated carbons have similar sugar decolourising effects to coal based active carbons. Unlike coal, bagasse does not contain sulphur (under normal conditions), eliminating the risks associated with formation of acid rain.
- The presence of inherent porosity in bagasse stemming from its fibrous nature makes it a better raw material than non-fibrous materials in terms of the kinetics of pore development. The importance of porosity is fully illustrated in Section 3.1. Bagasse is also available from sugar mills in a partially processed form compared to other precursors which undergo pretreatment such as grinding and milling. This involves expensive machines with high maintenance costs.
- Bagasse is a by product of the sugar manufacturing process and the sugar factories can use activated carbon to improve the colour of sugar, so it makes the bagasse-based activated carbon process attractive in terms of process integration. Sugar mills could provide an established industrial infrastructure for the activated carbon plant. Ko *et al* (2004) and Hui *et al* (2002) expressed the same sentiments for process integration – it lowers the total capital investment on equipment and reduces energy costs.
- Bagasse-based activated carbon production attracts several benefits to South Africa in terms of:
    - Environmental protection – sugarcane is viewed as a carbon sink unlike fossil fuels that contribute to global warming. The amount of carbon dioxide it uses for growth is much more than the amount produced during thermo-chemical treatment (Zanzi, 2001).
    - Uplifting the socio-economic status – the activated carbon production process will create employment.
    - The bagasse-based activated carbon process will provide an alternative adsorbent that is manufactured locally and help the country to save foreign currency for other uses.
    - Bagasse-based activated carbon could add value to the South African sugar, improving its competitiveness on the world market and bringing more foreign currency into the country.

Disadvantages of utilizing bagasse for activated carbon production include:

- Powdered bagasse-based activated carbon produced without using binders gives low yields, has a low abrasion resistance and therefore difficult to regenerate.
- Utilization of bagasse for production of activated carbon has SHE problems (Van der Poel *et al* 1998). Bagassiosis is an allergic reaction of the lung tissue to the presence of air borne *Thermoactinomyces sacchari* spores which are present in significant concentration in stored bagasse. The handling of bone dry bagasse can result in problems such as coughs, dysphomea, malaise and chest pains. Storage of humid bagasse containing 45-55% water (fresh bagasse) is hazardous because microbial activity releases alcohols, acids and heat which not only changes the quality of the fibrous components but may result in self ignition.
- Bagasse is bulky and hence its transportation to a processing plant from different sugar mills is generally uneconomic (Erlich *et al* 2005).
- Pelletising is one way to improve bagasse handling problems but the costs associated with purchasing and maintaining hammer mills, pellet mills and the binding agents could make the final product expensive (Erlich *et al* 2005)
- Bagasse is a very heterogeneous material both physically and chemically. Carry over of small bagasse particles in gas streams requires installation of expensive gas cleaning systems. Pelletising and screening are some examples of pretreatment processes done to reduce pollution due to particulate matter.

ACTIVATED CARBON CHARACTERISTICS AND USES

3.1. Activated carbon.

Activated carbon consists of a distorted three dimensional array of aromatic sheets with angular pores of molecular dimensions. According to the IUPAC (IUPAC, 1972), these pores can be classified as micropores (dp>2nm), mesopores (2nm<dp<50nm), and macropores (dp>50nm). The edge carbons with unsatisfied valencies create active sites for adsorption with heteroatoms.

Current applications include adsorption of gases (for recovery and ventilation purposes), separation of hydrocarbons (for recovery, processing and separation purposes), adsorption from solutions (for decolourising and purification purposes), and reactivity and catalysis. Active carbons works by adsorption - defined as the preferential accumulation of a dissolved substance (solute) at an interface (Holden, 1982). PAC and GAC are essentially the same except that during product screening, particle sizes less than 0.4mm are considered a poor filtration medium and usually sold as a powder. Powder is used entirely in liquid phase application on a once through basis, while granulated activated carbon can be reactivated by thermal or chemical treatment.

Activated carbons have unique characteristics that are dependent on the type of raw material and the processing method employed during manufacture (Allen *et al* 1998). Table 3-1 shows properties of some active carbons. The BET surface area represents the surface for adsorption (active sites) and the pore volume represents the density of tortuous micro-chambers.

Table 3-1 Properties of commercially available carbon (Valix *et al* 2004)

Manufacturer	**Application**	**Precursor**	**S_{BET} (m^2/g)**	**Pore volume (m^3/g)**	**Ash (wt%)**
Calgon	Gas phase	Coal	1050 – 1150	0.8	< 8
Norit	Gas phase	Peat	1100 – 1200	0.9	6
Calgon	Gas phase	Wood	1750	1.2	n/a
Westvaco	Liquid phase	Coal	900 – 1000	0.85	< 10
Norit	Liquid phase	Peat	750	n/a	6
Westvaco	Liquid phase	Wood	1400 – 1800	2.2 – 2.5	n/a

3.2. Sugar colour

Sugar solutions contain different colouring matters and their main sources are sugarcane and the sugar process. These colourants are classified into six main categories, namely:

- Plant pigments – principally consists of phenolics and flavanoids and they form coloured matter by oxidation reaction with amines (or iron) and enzymic browning reactions respectively.
- Caramels - non-nitrogeneous colouring substances formed by thermal decomposition of sugars
- Melanoidins – is the most intensively coloured category formed from nitrogenous colouring substances by reactions of reducing sugars with amino acids (Maillard reactions)
- ADPs of fructose – these are brown coloured substances formed by the thermal degradation of reducing sugars under alkaline conditions
- Colour precursors – these are colourless compounds which only form colour after undergoing reactions during processing and include amino acids and phenolic copmounds

The coloured bodies consist of both dissociated and non-dissociated compounds but the anion prevails. Table 3-2 shows the properties of cane sugar colourants.

Table 3-2 Summary of properties of cane sugar colourants (Davis, 2001)

Property	**Monomeric**	**Intermediate**	**Polymeric**
Composition	Mainly flavanoids	Factory colourants e.g. ADP	Factory colourant, e.g. caramels, melanoidins
Molecular weight	<1000	1000 - 2500	>2500
Ion	Neutral at low pH	Cationic below pH = 5 Anionic above pH = 6	Cationic below pH = 5 Anionic above pH = 6
Polarity	Less polar	Intermediate	Polar

Recent research by Barker and Ramsumer (2004) has confirmed that sugar colours in South Africa were influenced by cane varieties and geographical location of the cane field. A cane variety, N33 was reported the highest colour variety with over 20 000 ICUMSA units, about 5000 units above the second highest, N32 and up to 15000 units above the lowest colour N19 and N11. High colours of approximately 1.3 times were prevalent along the North Coast of South Africa compared to Midlands, Zululand and Durban North Coast. This helps to illustrate why particular active carbons perform differently in different countries (Smisek, 1970).

According to Zerban (1947) colourants influence:

- Sugar crystallization - The adsorption of colour during crystal growth retards the crystallization process and this increases with crystal growth as the impurities accumulate in the mother liquor.
- Sugar keeping quality – One way to prevent darkening of sugar products is to use the lowest possible temperatures, low pH and low keeping times.
- Sugar marketability - Dark coloured raw cane sugar is more expensive to refine and refineries would prefer lighter grades.
- Sugar fermentability - Molasses contains organic non sugars (colour bodies) and the amount of this impurity on the crystal surface can lead to fermentation reactions and darkening of raw sugar in storage.
- Errors in analysis - Sugar analysis using copper reducing methods could be misleading if other reducing agents are present (other than reducing sugars).

3.3. Sugar decolourisation processes

The diversity of sugar colourants and the different mechanisms of colour removal in terms of their physical and chemical properties is the main reason why optimum process combinations are used for effective colour removal. Currently the sugar industry uses for sugar decolourisation: Bone char (on a decreasing scale), PAC, GAC and Ion exchangers. A comparison of the different sugar decolourising processes is shown in Table 3-3. Activated carbon proves to be the best decolouriser by removing most of the coloured matter such as flavanoids, phenolics, caramels and melanoidins.

Table 3-4 illustrates some beneficial process combination for colour removal. Its important to note how different processes complement each other especially for effective colour removal (as denoted by C) and pH (as denoted by P). The first processes are listed horizontal and the second process listed down the second left column. A symbol (P) is shown where the pH of liquor from the first process is beneficial for the second process. Smisek (1970) reported that sulphitation improves the effectiveness of activated carbons and the optimum pH was about 4.5. However a compromise has to be reached between potential colour formation and loss of sugar when choosing the best operating pH. The Nchalo Mill in Malawi is a good example on how optimum process combinations can be of benefit to sugar processing. The factory changed from a sulphitation-phosphatation process to a phosphatation-activated carbon process resulting in marked improvements in sugar colours (Debwe, 2001).

Table 3-3 Comparison of decolourisation processes (Davis, 2001)

Process	Phenolics	Flavanoids	Melanoidins	Caramels	ADF products	Colour precursors
Activated carbon	✓	✓	✓	✓	×	
Carbonatation	✓ !	×	✓	✓	!	
Sulphitation	✓	✓	✓			✓
Phosphitation	×	×	✓	✓	✓	
Colour precipitation			✓	✓	✓	
Oxidative decolourants	✓	✓				✓
Ion exchange	×	×	✓	×	✓	

✓ - well removed × - poorly removed ! - formed in process

Table 3-4 Process combinations for colour removal (Davis, 2001)

Process		First						
		Carbonatation	Sulphitation	Phosphatation	Precipitation	Oxidation	Active carbon	Ion exchange
Second	Carbonatation	▨	NC	NC		CP	NC	NC
	Sulphitation	P	▨			X	NC	NC
	Phosphatation	X		▨	CP	C	NC	NC
	Precipitation	C	C	C	▨	X	NC	NC
	Oxidants	X	X	X	X	▨	NC	NC
	AC	C	CP	CP		C	▨	NC
	Ion exchange	P		X		X	C	▨

C – colour removal P – pH beneficial to the 2nd process X – not ideal NC – normally not considered

Blank cells – insufficient knowledge

3.4. Activated carbons for the sugar industry

The affinity of active carbons to different colouring matters depends on the physical and chemical structure, pore size and charge as discussed in Section 3.6. Active carbon has been successful in making white sugar from thick juice (syrup) that is comparable to refined white sugar. Apart from colour removal, treatment of syrup solutions with activated carbon also helps to increase surface tension, decrease its viscosity and this helps to improve rates of sugar crystallization and its separation in the centrifuges (Smisek, 1970). Completely exhausted carbon can be used for mechanical filtration, prefiltering turbid solutions. However for decolourisation of thick sugar solutions, improved mass transfer and solid-liquid contact can be obtained by operating the system at an elevated temperature. The diffusion of the colour components is a function of the temperature and viscosity of the sugar solution, and the molecular size of the colourants (Chen and Chou, 1993).

The effectiveness of carbons for removal of non sugars is shown in Table 3-5. The results show the favourable effectiveness of PAC compared to other adsorbents.

Table 3-5 Effectiveness of adsorbents for removal of non sugars (Smisek, 1970)

Adsorbent	Colouring matter	Colloids	Ash
Bone char	+	+	+
GAC	++	+	
PAC	+++	++	
Ion exchangers	++	+	+

However to further analyse the PAC system, its worth looking at its advantages and the disadvantages.

Advantages of PAC:

1. short contact times
2. small dosages of adsorbent
3. lower water and energy consumption
4. low labour requirements
5. flexible operation
6. plant easy to commission
7. low investment costs
8. low space requirements
9. no harmful waste waters when applied on an once through basis
10. low sugar losses by thermal decomposition because of the low contact time

Disadvantages of PAC:

1. the process can be messy
2. active carbons do not remove ash (especially Calcium)

3.5. Technique of decolourising with PAC

There are basically three techniques of contacting sugar solutions with PAC: contact batch application, continuous layer filtration and a combination of both methods.

3.5.1.Contact batch application

This is essentially a batch process. Activated carbon is mixed with sugar at 80 - 95°C for 15 – 20 minutes to establish equilibrium giving an 80% colour removal. The method is very flexible, dosage of activated carbon can easily be adjusted to suit colour of juice, and the decolourising effect is uniform and can utilize low quality carbon though in large quantities (about ten times the continuous layer filtration). The carbon is recovered from solution by pressure filtration at about 2 – 4 Bar gauge pressure.

In a sugar factories working with only one liquor line, a two stage countercurrent arrangement can be utilized where active carbon from the first stage is used for pretreatment before further decolourisation with fresh carbon.

3.5.2.Continuous layer filtration

This is principally a filtration process of the sugar solution through an activated carbon layer. The leaf filter is coated with a filtering aid and then a uniform carbon layer of about 10 – 15 mm thick. The solution is required to flow uniformly because stoppages or sudden changes in flow can break the carbon layer. High pressures of up to 4 Bars gauge can be used to give about 80% decolourising effect. The effectiveness of the bed gradually decreases until a certain limit warranting change. This method is adopted for carbons with high decolourising capacity.

3.5.3.Combined method

This method utilizes the advantages from the two above methods. The filter is precoated with a layer of fresh, non regenerated carbon and additional carbon is added to the solution to be filtered.

All methods stated above require a re-filtering stage to trap entrained activated carbon.

3.6. Properties of activated carbon for sugar decolourisation

The following are some of the physical, chemical and surface properties for good sugar colour removal. It is important to know the different colour types because they exhibit different chemical and physical characteristics in solution.

3.6.1.Physical properties

The most important physical properties of activated carbon are particle size, bulk density and abrasion resistance.

The particle size of activated carbon influences the kinetics of adsorption, and the filtration process (Ahmedna *et al* 2000). PAC mixes intimately with liquid giving better adsorption kinetics in terms of mass transfer than GAC. However small PAC may cause excessive pressure drop in the filters.

The bulk density of carbon influences the filtration process. It determines the quantity of filter cake to be collected and the amount of sugar loss due to residual liquid in the cake. A bulk density of about 0.5g/ml is adequate for good filtration and even cake formation (Ahmedna *et al* 2000). Bagasse based carbons have a bulk density of 0.10 g/ml. Bulk density is important for GAC used in column modes and generally a higher bulk density reduces frequency of regeneration because it will hold more adsorbate per unit volume. Bulk density is also very closely related to and affected by particle size (Ng *et al* 2002).

The activated carbon should have sufficient abrasion resistance to minimize attrition during use since this affects the filtration process. This is also an important property when considering regenerating the activated carbon. Bagasse based activated carbon has a very high attrition (93%) which indicates its low material strength. High attrition can cause filtration problems by causing fine particles to accumulate on the filters. This should impact on the mode of application of bagasse-based active carbon.

3.6.2.Chemical properties

Ash is an impurity and consists mainly of mineral matter like silica, calcium, magnesium, aluminum, and iron (Ahmedna *et al* 2000). Low ash content in sugar is an important quality component hence it is undesirable to have ash leaching from the carbon into the sugar. The total ash comes with the activated carbon precursor and in varying compositions. Ash causes uneven heating during crystallization, catalysis of adverse reaction and competitive adsorption (Ahmedna et al 2000), binds sucrose and increase molasses production (Smisek, 1970).

A pH of 6 – 8 is the most desirable for sugar colour removal. Acidic conditions cause sugar loss due to inversion while alkaline conditions cause colour development.

3.6.3.Surface properties

The surface properties of activated carbons are characterized by surface area, porosity and surface chemistry.

A good adsorbent should have a high surface area and this can be as high as 1500m^2/g. Surface area is closely related to the number of active sites. Since the number of active sites cannot be measured, surface area becomes an important design factor for adsorption of compounds from sugar liquor.

Porosity is divided into macropores, mesopores and micropores. Macropores are important for transportation of adsorbate to the mesopores and subsequently the micropores. Micropores constitute the highest surface area in activated carbon. However good mesoporosity development is needed for adsorption of sugar colourants. Sugar colourants are made up of mixtures of compounds with varying molecular size and most of these are in the mesopore size region.

The surface chemistry of activated carbons is influenced by presence of heteroatoms and these atoms are either derived from the precursor or attained through the process route. Common heteroatoms in activated carbon include oxygen, hydrogen, chlorine and sulphur, but the C – O structures are the most important, they make activated carbon acidic or basic. The raw sugar colourants – a complex mixture of polydispersed compounds of differing molecular size and net charges, are predominantly anionic and therefore the diversity of the functional groups on the carbon surface influences the electrochemical adsorption mechanism (Ahmedna *et al* 2000). The discrepancies between expected performance of an activated carbon, based upon surface area and pore-size distribution data, and actual adsorptive capacity can often be explained by surface chemistry.

3.7. Other uses of activated carbon in liquid application

3.7.1.Food industry

Activated carbon is used to improve the colour of beverages, oils and fats. In case of brandies, active carbon is used to improve the flavour by removing undesirable flavours picked up from processing and storage. Active carbon is used to remove fusel oil from wines and spirits (Bansal, 1989; Smisek, 1970). For economic reasons active carbons are mixed with cheaper adsorbent under controlled conditions to decolourise oils and fats.

3.7.2.Chemical industry

Special activated carbon is used in the pharmaceutical industry for decolourising organic substances. The decolourising effect of the carbon depends on the solvent used and falls along the series, water – methanol – ethanol – ethyl acetate – acetone – chloroform (Smisek, 1970).

Activated carbon is used at small scale in the laboratory for isolating natural substances from dilute solutions. However the materials are strongly bonded to the carbon and their elution is therefore costly and with considerable losses. This explains the minimal application in this respect (Smisek, 1970).

Activated carbon is used in gold extraction from cyanide extracts. The use of activated carbon for gold recovery dates back to 1880 (Bansal, 1989). Activated carbon is used to remove contaminants such as bacterial toxins from hypodermic syringes. Contaminated solutions cause acute body reactions causing a rise in body temperature (Smisek, 1970).

Activated carbon is used in electroplating baths to remove organic impurities which accumulate and impair the quality of the electroplated surface. Organic impurities include emulsified oils and fats, decomposition products of melting agents and brighteners, etc (Bansal, 1989).

3.7.3.Water and wastewater treatment

Activated carbon is used to remove organics from drinking water and wastewater. These organics are derived from municipal discharge, urban runoff, natural decomposition of vegetables and natural matter (Bansal, 1989). Industrial effluent water often contains harmful and toxic material and activated carbon is used to treat it. For example, oil removal from refinery wastewaters. Other harmful wastes where activated carbon is used include effluent associated with electroplating, manufacture of fungicides and insecticides (Holden, 1982). Activated carbon is used in potable water to improve its tests and odour, and at the same time remove trace halogenated compounds.

3.7.4.Catalysis

Activated carbon is used to convert excess chlorine in the final phase of potable water treatment by filtration through a bed of activated carbon. The surface reaction gives out carbon dioxide and hydrochloric gas. Activated carbon is also used as a catalysts in that in the presence of oxygen it catalyses the oxidation of Fe^{II} to Fe^{III}. In the presence of the reducing agent such as SO_2 carbon catalyses the reverse reaction, i.e., the reduction of Fe^{III} to Fe^{II}.

LITERATURE SURVEY ON THE MANUFACTURE OF ACTIVATED CARBON

4.1. Basic flow sheet

Most raw materials can be processed into activated carbon by the most direct and economical route as shown in Figure 4-1. Though the type of activated carbon depends on type of raw material, the nature of the product can be varied by reconstituting the raw material, or by partial carbonization and then reconstitution or by compresing the raw material before carbonization or after activation (Bansal, 1988) Activation may involve a physical or chemical method and sometimes a combination of both methods. Hence the production of activated carbon can involve a single stage, two stages or even three stages. The final product quality depends on the carbon precursor, the pyrolysis and activation conditions and the activating agent. Many papers and patents have been written on the manufacture of bagasse-based activated carbon as discussed later in this section, however commercial application is yet to be realized. The closest attempt to commercial application is a paper by Ng C *et al* (2002).

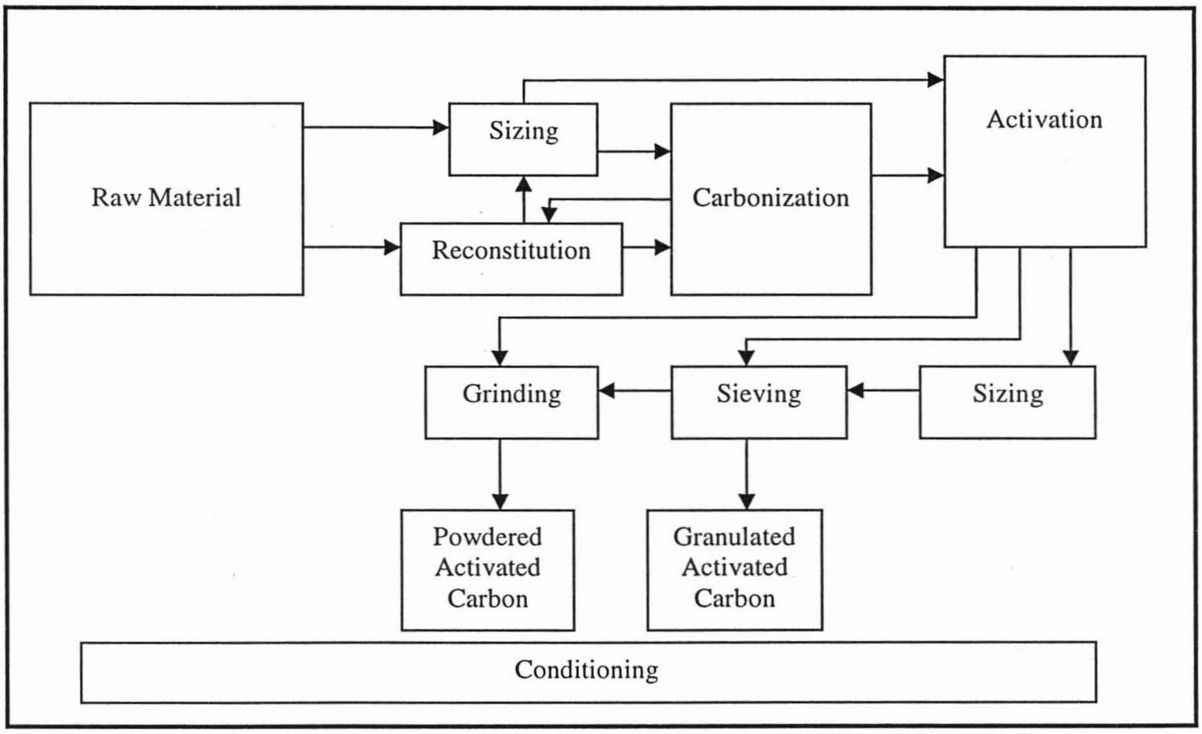

Figure 4-1 Basic flow diagram for active carbon production (Bansal, 1988)

4.1.1. Laboratory scale

Literature review shows that activated carbon can be made from bagasse by chemical activation - Ruiz & Rolz (1971); Yousef (1980); Girgis *et al* (1994); Lavarack (1997); Xia *et al* (1998); Castro *et al* (2000); Sirichote *et al* (2002) or physical activation - Suarez *et al* (1968); Bernado *et al* (1997); Xia *et al* (1998); Johns *et al* (1998); Minkova *et al* (2000); Ahmedna *et al* (2000); Dermstadt *et al* (2001); Krishnan (2002); Juang *et al* (2002). Examples of physical activation methods used to make bagasse- based active carbons are given in Table 4-1.

Table 4-1 Laboratory production methods for active carbon.

Author	**Carbonization**	**Activation**	S_{BET} (m^2/g)
Xia *et al* (1998)	700 - 800 °C in N2	1hr at 700 - 800°C with steam	947
Juang *et al* (1996)	450°C in N2	2h at 750 - 840°C with steam	607
Lutz *et al* (1997)	380°C for 3hrs	850 - 900°C with steam	1035
Bernado *et al* (1997)	300°C in N2	1h at 800°C with steam	1394
Pendyal *et al* (1999)	750°C in N2	4 - 20h at 900°C with $P_{CO_2} = 0.13$	< 300
Darmstadt *et al* (2001)	500°C (8kPa)	2h at 850°C with steam	1579
Valix *et al* (2004)	160°C for 2h with acid	1 - 15h at 900°C with CO2	1146

4.1.2. Patented processes

The patented processes take bagasse as one of the lignocellulosic materials that can be used as a raw material. These patents include Shinomiya *et al* (1974) - US Patent No 3 835 064; Matthews *et al* (1994) - US Patent No 5 276 000; Yan *et al* (1996) - US Patent No 5 538 932; John *et al* (2003) - US Patent 6 537 947.

Shimoniya *et al* (1974) invented a better method of making chemically activated active carbons by using a conveyor belt furnished with a thin sheet of a corrosion inhibiting organic substance. A heated plate was placed between the conveyor and the organic substance. Afterwards the feedstock was put on the conveyor and placed in a furnace. Relatively low temperatures of about 400°C were used to produce a high quality carbon.

Yan *et al* (1996) produced hard activated carbon from lignocellulosic material by making char at 300°C, grinding it and pelletising the agglomerated acid char by extrusion. Finally activation was accomplished by heating the pelletised material under controlled conditions preferably 450 - 500°C. The final product had a surface area of 2420 m^2/g, particle density of 0.48g/cm^3 and 60% of mesopore volume.

John *et al* (2003) prepared GACs from carbonaceous material for use in adsorption of metals. The process involved carbonization under inert conditions at 700 - 750°C for 1 – 2 hours, then using carbon dioxide or steam activation at 800 - 950°C for 3 – 12 hours and subsequent oxidation with air at 260 - 400°C for 3 – 6 hours. The S_{BET} of activated carbon produced at 57% burn-off was 700m^2/g, a bulky density of 0.35g/cm^3 and 0.70 – 0.80 mol of copper per g of carbon.

4.2. Drying Bagasse

Bagasse drying involves the evaporation of water and its subsequent separation from the solids. Mass transfer from the drying solids is presumably a function of the size, shape and the disposition of the solids' particles and the ease with which the liquid and vapour can migrate from the pores and capillaries within the solid to its bulk external surface (Moss *et al* 1971). According to Cheremisinoff (1986) and Schlaudraff (1983), there are three stages in thermal drying:

1. The initial drying is short and accounts mostly for the sensible heat to raise the temperature of the wet bagasse to drying temperature for conduction drying and to the wet bulb temperature of the drying medium in the case of convective heat transfer (low temperature drying).
2. The steady state drying is the longest and occurs at constant temperature. The drying mechanism involves the evaporation of surface moisture.
3. The final drying occurs when the solid surface is partially saturated and hence surface moisture is lost faster than it is replaced. The solid/ gas interface temperature increases because the latent heat cannot be transferred from solid to the gas phase as rapidly as sensible heat is received from the heating medium and the dying rate decreases.

The effectiveness of a thermal drying process is governed by four fundamental factors:

1. Moisture dispersion within material, allowing maximum exposure of moisture surfaces to be heated.
2. Large temperature differentials – high gas temperatures are required for rapid drying
3. Maximum agitation of the material to increase the rate of heat transfer.
4. Particle sizes must be at a minimum to increase the surface from which moisture can be evaporated and allow the moisture to reach the surface for drying.

4.2.1. Hot flue gases

The industrial challenges due to high energy costs and the need to sell in the global market has helped renew interest in utilizing energy from flue gases. Cheremisinoff (1986) states that the principal cost in drying operations is heat and unlike using steam, the cost of using flue gases eliminates the costs of raising the earlier. This means that the heat required to dry bagasse using hot gases consists of:

- heat to raise bagasse (in wet feed) to the temperature of product as it leaves the dryer
- heat required to raise water temperature to point of evaporation plus latent heat of evaporation
- heat to offset heat losses

Flue gases by the virtue of being at higher temperature than surroundings and having a higher mass flow rate poses considerable available energy which if not utilized properly will lead to huge undesirable energy loss (Reddy et al 2002). Studies elsewhere have shown process flue gases as a cheap alternative source of energy for drying solids (Zabaniotou, 1999; Hugot, 1986; Van der Poel, 1998; Chen and Chou, 1993).

Bagasse drying using flue gases is practiced in some sugar mills to improve boiler efficiency. This is illustrated in Table 4-2. Flue gas has a specific heat capacity of 1.34 kJ/ kg.°C at 100°C compared to air with 1.005 kJ/ kg°.C (Schlaudraff, 1983). The predominant drying mechanism in direct dryers is convection, and conduction in indirect dryers.

Table 4-2 Review of Bagasse Dryers utilizing excess heat from stacks (Gamgami, 1991)

Sugar Factory	**Year**	**Type**	**Dimensions**		**Bagasse rate, t/h**	**Water content**		**Remarks**
			D(m)	**L (m)**		**in %**	**out %**	
San Antonio Brazil	1980	Tower pneumatic	-	-	4.52	40.0	6.0	Exhaust gas 220°C
Davies Hawaii Inc	1980	Rotary drum	3.6	9	65.0 10.7	50.0 35.0	35.0 16.0	
Hilo Cost, Hawaii	1980	Rotary drum	4.52	9	72.0	48.0	35.0	
Central Azucarero Philippines	1982	Towers pneumatic	-	-	24.0	52.0	24.0	
Central Aidsisa Philippines	-	Rotary drum	3.3	12	45.0	54.0	48.0	Exhaust gas 258°C
Central Victoria Philippines	-	Rotary drum	2.4	15.7	13.0	50.0	45.0	
Zaio Morocco	1985	Rotary drum	3	16	14.0	53.0	40	Exhaust gas 220°C

4.2.2. Indirect drying method

This method utilizes conduction heat transfer and wet bagasse is dried with hot gases by heat conduction via a wall. The vaporized water is removed independent of the heating medium. According to Zandersons *et al* (1999), the higher the bagasse drying temperature the shorter the duration of drying. The results showed that it is possible to get moisture content of 1 – 2% by drying bagasse at 200°C in a rotary drum at wall temperatures of 320 - 600°C for 5 – 80 minutes depending on the amount of wet feed. However in sugar mills, the exploitable drying temperature is between the boiler outlet flue gases temperature range (typically 170 - 200°C) and a saturation temperature of 70 - 80°C. This range represents a heat load of about 100 – 420kJ/kg depending on the amount of moisture condensed (Schlaudraff, 1983). In practice most of the heat is recovered as latent heat.

4.2.3. Direct drying method

This method of drying utilizes convection heat transfer and it is accomplished by direct contact between wet bagasse and hot gases. The vaporized water is removed by the hot gases. To achieve reasonable drying rates, the required gas temperatures should be in the 315 - 480°C range and the gas should exit at 20 - 50°C above the dew point (Sofer and Zaborsky, 1981). This is consistent with Zabaniotou *et al* (1999) who used exhaust gases from burning pyrogas to dry 1.33 tons/h of biomass by 15 mass % on dry basis in a rotary kiln. The exhaust gases going into the dryer were at 330°C and 120 - 160°C at the exit. The main challenges faced by using combustion gases for direct drying are the problems of soot, the dew-point of the combustion gases and subsequent carryover of finer and dried bagasse particles because of finer preparation of cane for diffusion.

4.2.4. Direct flame dryers

According to Perry (1997) scoop systems are provided for introducing a feed component/fuel through the shell at some intermediate points. Ports are installed in the shell for admitting combustion air at points beyond the hot zone; these are used for burning combustibles (pyrolysis and activation gaseous products) from the material being processed. Firing may be done from either side of the kiln depending on whether its co-current or countercurrent operation, and sometimes the feed is mixed with the fuel and burned as it moves along the kiln. Gaseous, liquid and solid fuels may be used.

4.3. Pyrolysis of bagasse

Pyrolysis of bagasse is an energy intensive reaction that reduces the solid substrate to a solid product (char), liquids (tars and condensables) and gases (CO, CO_2, CH_4, etc). The most important factors that determine the yield and quality of char are heating rate, peak temperature and hold time. It is in this stage that the fixed carbon skeleton is created and the initial phases of pore development arise, which is further improved during activation (Devnarain, 2003). Bagasse is a matrix of three components, lignin, hemicellulose and cellulose. Compared to the knowledge on cellulose pyrolysis, considerably less is known about pyrolysis of the other two components and very little about lignocellulosic matrix in general (Roberts *et al* 1980). Consequently the mechanism that occurs during bagasse pyrolysis is complex and difficult to determine due to the large numbers of complex reactions that occur and the broad range of products that have to be accounted for. (Milosavljevic *et al* 1996; Garcia-Perez *et al* 200). An example of the pyrolysis chemistry of bagasse is given in Table 4-3.

4.3.1. Bagasse pyrolysis chemistry

Table 4-3 Pyrolysis of pulverized bagasse in Helium (Rodriguez *et al* 1993)

Temperature	**Activity**
25 – 110	Drying
110 – 170	Decomposition of polysaccharides and evaporation of bound water in colloids (endothermic)
170 – 250	Breaking weak bonds in OH, COOH and methoxyl to give CO, CO_2, H_2O (endothermic)
250 – 280	Decomposition of hydrocarbons (hemicellulose + cellulose)
280 – 310	Liberation of hydrocarbons and hydrogen plus decrease in CO and CO_2 yield
310 – 450	Decomposition of lignin and extractable substances (exothermic). *Peak devolatilisation occurs at 350°C.
450 – 700	*Predominantly degradation of lignin to give char. Mass loss is very low, about 3 – 4%.
450 – 900	Breaking C – C chains and coke residues formed (endothermic)

* Katyal *et al* (2003)

Nassar *et al* (1996) defined the thermal degradation of bagasse as a two-stage process involving volatilisation and carbonization. Further investigations (Nassar, 1999) revealed that the thermal degradation of bagasse at low heating rates produces two main mass loss regimes, one for the decomposition of hemicellulose and onset of cellulose decomposition in the lower temperatures and the other for the final stages of cellulose decomposition and the decomposition of lignin. During this low temperature regime the yields of carbon, water and methane are very high and later higher temperatures yield more of carbon dioxide and carbon monoxide. On the other hand, secondary tar degradation reactions become active for temperatures above 420°C with carbon monoxide as the main product followed by methane and ethane. The reactions that occur during the degradation of bagasse are divided into cleavage of C – H, C – O, and C - C bonds, dehydration, decarboxylation, decarbonylation reactions and the formation of C – C, C = C, and C – O, carbonyl and carboxylic groups (Garcia-Perez *et al* 2001). The production of hydrogen at low temperatures (below 850K) is negligible for all biomass and its generation rapidly rises above 850 – 900K. The relatively high amount of carbon dioxide in the off-gases is due to the presence of a high amount of oxygen in the feedstock (about 43 wt% for bagasse) resulting in a gas with a low heating value. This is confirmed by ultimate analysis results on bagasse char as a function of temperature from 200 - 500°C (Bilba and Quensanga, 1996).

4.3.1.1. Cellulose pyrolysis chemistry

Many kinetic models have been proposed for the decomposition of cellulose and examples are given below:

- the Broido-shafizadeh Model - Broido *et al* (1975)
- the Waterloos model - Piskorz *et al* (1989)
- the Diebold model – Diebold (1994)
- the Varhegyi - Antal model - Varhegyi *et al* (1999)
- the new model for low temperature cellulose pyrolysis - Wooten *et al* (2003)

The models have increased in complexity in an attempt to fully describe the distribution of decomposition products under a variety of heating conditions and to predict the rates of evolution of products. Nevertheless most modelers still consider the mechanism as a simple first order within reasonable accuracy. All the models listed above agree that the thermal degradation of cellulose proceeds in two directions, the formation of levoglucosan and glycoaldehyde (Antal and Varhegyi, 1995). Zandersons *et al* (1999) states that low heating rate promotes dehydration reactions of cellulose and thus cyclic structures are formed which act as charcoal aromatic precursors during the 350 - 400°C heating range. The degradation of cellulose occurs by fragmentation through random scission of the macromolecular structure accompanied by the generation of volatiles (Shukry *et al* 1991). Cellulose is the dominant component of bagasse and can therefore serve as a representative model compound for bagasse thermal decomposition: according to Antal (2003), the approximate stoichiometric equation of the decomposition of cellulose at atmospheric pressure is:

$$C_6H_{10}O_5 \rightarrow 3.74C + 2.65H_2O + 1.17CO_2 + 1.08CH_4$$

In comparison, Klason *et al* (1909) gave the equation:

$$C_6H_{10}O_5 \rightarrow 3.75CH_{0.60}O_{0.13} + 2.88H_2O + 0.5CO_2 + 0.25CO + 1.08C_{1.5}H_{1.25}O_{0.38}$$

Where the first product is charcoal and the last is tar. Pyrolysis quickly transforms bagasse into a tarry vapour containing complex soup of organic compounds mixed with noncondensables (CO, CO_2, H_2, CH_4 and heavy hydrocarbons) at temperatures between 250 and 400°C.

4.3.1.2. Hemicellulose pyrolysis chemistry

There are considerably less publications on the decomposition of hemicellulose materials (Varhegyi and Antal, 1989). Hemicellulose undergoes degradation reactions of depolymerisation, hydrolysis, oxidation, dehydration and decarboxylation reactions to yield volatiles and char. The decomposition reaction is usually described by a first order reaction. However most of the hemicellulose does not yield significant amounts of levoglucosan and ends up in the volatiles. Shafizadeh *et al* (1968) reported hemicellulose as the least stable of the three components making the bagasse matrix. The hemicellulose degrades at 200°C to around 260°C.

4.3.1.3. Lignin pyrolysis chemistry

Lignin is the most thermally stable of the three components of bagasse and thermally degrades at temperature above 300°C; cellulose and hemicellulose thermally degrades below 280°C (Rodriguez *et al* 1993, Nassar and Mackay, 1984). It consists of phenolic polymers containing hydroxyl, carboxyl and carbonyl groups (Lin, 1993). According to Mok *et al* 1992, there is a strong correlation between the lignin content in biomass and the char yield. Pyrolysis of lignin yields phenols from cleavage of ether and C – C linkages and produces more residual char than does pyrolysis of cellulose. Dehydration temperatures around 200°C are primarily responsible for thermal degradation of lignin. Around 300°C, aliphatic side chains start splitting off from the aromatic ring. Finally C – C linkages between structural units is cleaved at 370 - 400°C. The degradation of lignin is an exothermic reaction with peaks occurring at between 225°C and 450°C depending on the purging medium, nitrogen or air.

4.3.2. Pyrolysis products and operating conditions

Devnarain *et al* (2003), Katyal *et al* (2003) and Bilba and Quensanga (1996) studied pyrolysis of bagasse by varying peak temperature and hold time. Though hold time at peak temperature is important, the Arrhenius behaviour of the pyrolysis kinetics establishes the temperature as the controlling variable (Antal, 2003). Encinar *et al* (1997) reported that the products of biomass pyrolysis are numerous and their nature depends on operating conditions. From thermograms, the reduction in volatile matter is low below 300°C and loss is mainly due to water and extractive components. The rapid drop in volatile content between 300 and 500°C is due to decomposition of cellulose, hemicellulose and lignin (Devnarain, 2003, Katyal *et al* 2003). Table 4-4 shows the characteristics of bagasse char produced by Devnarain (2003) at pyrolysis temperature of 680°C, an average heating rate of 10°C/min and a hold time of 1hr at peak temperature. The BET surface area is about a third of the commercial carbon (Norit PN2) illustrating the importance of the inherent porous nature of bagasse fibre for further porosity development in active carbon.

Table 4-4 Bagasse char produced (Devnarain, 2003)

Parameter	Units	Value	Method used
Total Surface Area	m^2/g	331.46	Single Point
Total Surface Area	m^2/g	320.03	BET
Total Surface Area	m^2/g	423.50	Langmuir
Micropore Surface Area	m^2/g	271.79	t-plot
External Surface Area	m^2/g	48.24	t-plot
Cumulative Surface Area	m^2/g	28.47	BJH Adsorption[1]
Cumulative Surface Area	m^2/g	26.74	BJH Desorption[1]
Total Pore Volume[2]	m^3/g	0.1682	Single Point
Total Pore Volume	m^3/g	0.1263	t-plot
Cumulative Pore Volume	m^3/g	0.0482	BJH Adsorption[1]
Cumulative Pore Volume	m^3/g	0.0453	BJH Desorption[1]
Average Micropore Diameter	Å	21.074	Single Point / BET
Average Mesopore Diameter	Å	67.67	BJH Adsorption[1]
Average Mesopore Diameter	Å	67.80	BJH Desorption[1]

[1] between 17 and 3000Å diameter

[2] pore volume of pores less than 816.1Å diameter and $P/P_o = 0.0976$

Figure 4-2 shows a Scanning Electron Micrograph (SEM) of bagasse char. The micrograph verifies the rudimentary pore structure of the char.

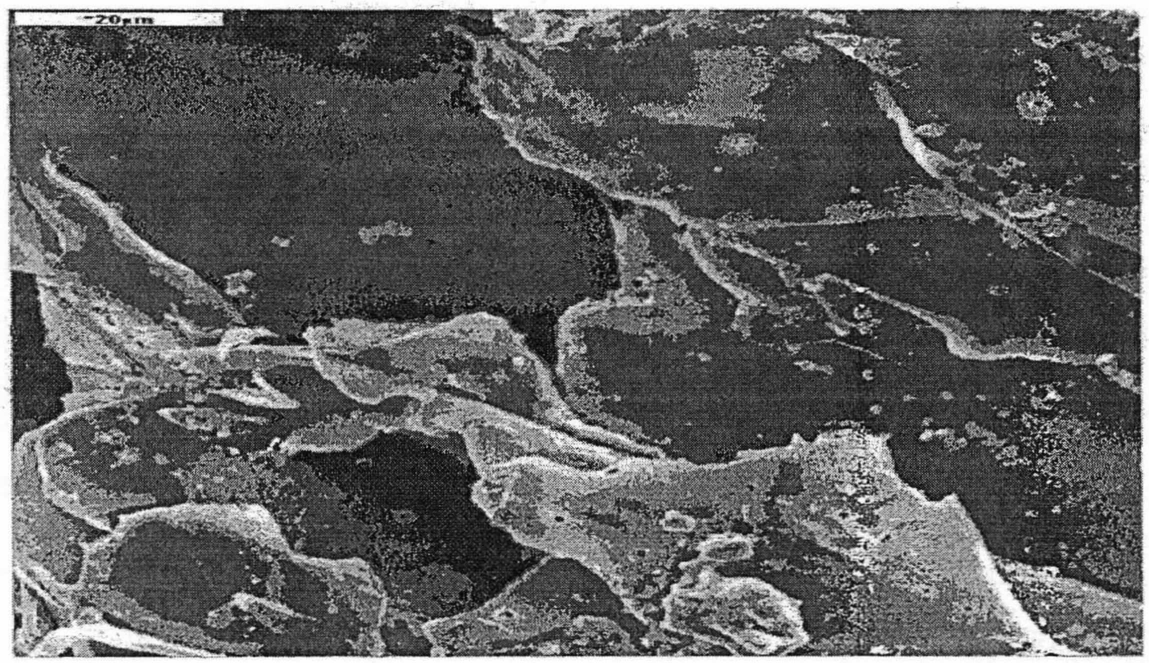

Figure 4-2 A SEM of bagasse char (Devnarain, 2003)

The two most important quality parameters of char for active carbon production are yield and reactivity. The char yield and reactivity is influenced by:

- Temperature: Treatment of biomass at high temperature increases the presence of inorganic elements at the surface due to migration of inorganic elements as a result of the thermal conversion process (Bonelli *et al* 2001). Antal (2003) reported that peak temperature has a strong influence on the pore structure, surface area and adsorptive capacity of the charcoal. The maximum char yield produced by the carbonization process is said to approach a theoretical value referred to as the thermochemical equilibrium limit (Antal, 2000).
- Residence time: High residence time increase contact time between tar and char resulting in production of secondary char. Secondary char probably encapsulates the ash and hinders its catalytic effect hence reduce char reactivity.
- Particle size: Higher temperatures and small particle sizes are related to high heating rates. Low heating rates encourage thermal cracking of volatiles and deposition of carbon in the pores and this reduces reactivity of char. Higher heating rates decrease char yield resulting in higher ash content in the produced char, favouring higher reactivity (Zanzi, 2001).
- Heating rate: Katyal *et al* (2003) studied the effect of heating rate on char and volatiles yield and concluded that it was insignificant and almost non existent for peak temperature above 400°C. However heating rates influence the kinetics of pyrolysis causing rapid evolution of volatiles above 400°C below which the higher residence time of volatiles inside char promotes higher char yield.

The composition of the pyrogas is also influenced by temperature, residence time, and particle size. Higher peak temperatures, residence times and smaller particles favour cracking of hydrocarbons in the pyrogas resulting in an increase in hydrogen. The high porosity of the bagasse ensures that the gases leave the solid particles faster and this result in increased residence time of gases in the reactor and subsequently cracking of the gases. As discussed in the section 4.3.1, the production of hydrogen is negligible for all biomass and carbon dioxide is the main component of pyrogas during thermal degradation of biomass at 850K as shown in Table 4-5.

Table 4-5 Gaseous products of pyrolysis - volume% basis (Di Blasi *et al* 1999)

	wood	**rice**	**straw**	**Olive husks**	**Grape**	***Bagasse**
Carbon dioxide	59	60	62	67	76	48.2 – 56
Carbon monoxide	34	32	28	23	14	28.6 – 31.8
C_2+ hydrocarbons	1.6 – 3.0	1.6	1.6 – 3.0	1.6 – 3.0	3.0	0.9 – 1.5
C_3 hydrocarbons						1.3 – 2.1
Hydrogen	0.1 – 0.5	0.1 – 0.5	0.1	0.1 – 0.5	0.5	1.1 – 2.4
Methane						2.2 – 6.7

* Garcia-Perez *et al* (2002)

4.3.3. Effect of carbonization on activation

During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic degradation of the bagasse and freed atoms of elementary carbon are grouped into graphitic crystallites (Smisek, 1970). Manocha (2002) reported that the basic microstructure of the char with microporosity is formed around 500°C. Devnarain (2003) reported that the transitions between microporosity to mesoporosity in South African bagasse chars at a heating rate of 10°C/min occurs in the region 500 - 900°C. Peak temperatures in the range 650 – 700°C produced char with the highest microporosity (and lowest mesoporosity) which is an important prerequisite for physical activation. Activation would help enlarge the micropores to mesopores while mesopores would generate macropores which are of little significance to the active carbons. Therefore the ideal conditions for pyrolysis in the making of active carbons should be in that temperature range. Other researchers have produced comparable results at pyrolysis temperatures ranging from 700 - 800°C (Katyal *et al* 2003; Pendyal *et al* 1999; Minkova *et al* 2000; Xia *et al* 1998; Zandersons *et al* 1999).

4.4. Activation of bagasse char

The main purpose of activation is to enlarge diameters of pores which are created during carbonization process and also to create new porosity thus giving a well developed and readily accessible pores structure with large internal surface area (Manocha, 2003). The product of carbonization is practically inactive, and activation can be visualised as interaction between the activating agent and the carbon atoms which form the structure of intermediates carbonized products resulting in useful large internal surface area with interconnecting pores of desired dimensions and surface area groups (Galiatsatou *et al* 2001). Activation is a two stage process mainly involving the nucleation of new pores and widening of existing ones to give a well developed pore structure. The adsorptive potential of the final active carbon is either developed at the initial stage of activation, or during the second stage, or evenly through the whole process. In the end, active carbons have internal surface areas in the range 500 – 1500 m^2/g, and it is this large area that makes them effective adsorbents (Wigmans, 1989). There are two methods of carbon activation, either by physical or chemical means. Physical activation involves partial or controlled gasification with oxidizing gases, e.g. steam, carbon dioxide and air. Chemical activation incorporates both carbonization and activation by thermal decomposition of bagasse impregnated with chemical activating agents such as zinc chloride. The extent of activation is measured by the degree of burn-off of the carbon material as shown in Table 4-6.

Table 4-6 Pores types and degrees of burn-off (Dubnin and Zaverina, 1949)

Degree of burn-off (%)	Pore type	Pore size
< 50	Micropores	< 2nm
> 75	Macropores	> 5nm
50 – 75	Mixed pores	All types

4.4.1. Chemical activation method

The raw material is impregnated with the activating agent in the form of a concentrated solution usually by mixing or kneading followed by extruding and then pyrolysis in a rotary kiln between 400°C and 800°C under inert conditions (Devnarain, 2003). The most widely used chemicals are phosphoric acid, zinc chloride, sulphuric acid, chloride salts of magnesium and ferric iron, sodium carbonate, sodium and calcium hydroxide and potassium sulphide. The chemicals act as dehydrating agents and inhibit the formation of tar, acetic acid and methanol (Manocha, 2003). The advantages of chemical activation is that it is a single step, gives high carbon yield (less weight loss) and it occurs at a lower process temperature compared to physical activation. While relatively low temperatures are used, the disadvantage of chemical activation is that the porous structure is dominantly micropores and narrow mesopores (Allen *et* *al* 1998). In general, chemical treatment is associated with high operating costs and disposal problems. The following points are inherent in chemical activation:

- the chemical corrodes the equipment
- the chemicals are not easily recoverable and may be lost in the following ways:
    - corroding metals and hence wasted
    - vaporized at high temperatures
    - lost as waste during washing of active carbons
- Chemical activation requires the use of expensive equipment.

Chemical activation is used exclusively for biomass-based active carbons which have very high amounts of volatiles. The process is carried out in the range 400 - 800°C; temperatures lower than those required for physical activation. The degree (coefficient) of impregnation is an important factor in chemical activation. It is defined as the weight ratio of the anhydrous activating salt to the dry starting salt. The degree of impregnation dictates the amount of salt in the feedstock and this equals the volume of pores which are freed by its extraction. The chemical carbons obtained in the powdered form are products of high activity and adsorption and are generally used for decolourisation (Bansal, 1988).

4.4.2. Physical activation method

Most commercial carbons are made by steam activation. Initial increase in surface area is due to formation of new porosity or opening of existing pores previously blocked. As gasification progress and conversion reaches higher values there is a decrease in surface area due to collapse of pores as a consequence of the gasification of the pore walls. The activation mechanism can be described as follows:

1. At burn-off below 10%, the active oxygen burns away tarry-material trapped in pores and more accessible single aromatic sheets of carbon thereby initializing pore development.
2. The active oxygen burns away carbon from pore walls resulting in an increase in wider pores (meso- and macropores) and this reduces the volume of micropores.

The reaction of carbon with steam is as follows:

$$C+H_2O \rightarrow CO+H_2 \quad (1) \qquad \Delta H = +117\ \text{kJ mol}^{-1}$$

Similarly, the reaction of carbon dioxide with carbon can be expressed as

$$C+CO_2 \rightarrow 2CO \quad (2) \qquad \Delta H = +159\ \text{kJ mol}^{-1}$$

Under practical conditions (above 800°C), the water gas shift reaction is at equilibrium with equilibrium constant between 0.5 and 1.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

Reactions (1) and (2) are important reactions during gasification though the first one is the primary reaction. Carbon monoxide and hydrogen influence the gasification reaction as inhibitors. In practice, air is supplied to provide the energy requirements for gasification by burning off syngas and this indirectly helps speed up the reaction by decreasing partial pressure of the inhibiting products (Wigmans, 1989). It is important to note that air is always present during gasification but it has no direct contact with carbon during gasification due to mass transfer limitations as a result of dynamic processes occurring in the gas film surrounding the carbon. Otherwise all the carbon would burn away since the reaction of air with carbon at temperatures above 800 °C is more than 100 times faster than steam or carbon dioxide. However 800 - 850°C seems to be the optimum temperature level for activating carbon without noticeable shrinking core behaviour (Wigmans, 1989).

The gasification reaction takes place in a series of consecutive steps that involve diffusion, transport and chemical reactions of gaseous reactant. The oxidizing agent diffuse through tortuous pores within the carbon char and this creates a variation in concentration of the oxidizing agent. The mechanism and reaction rate equations for activation with carbon dioxide and steam are discussed in detail by Smisek (1970).

4.4.3. Steam activation

The steam flow rate affects mainly the mass transfer coefficient through the gaseous film surrounding the carbon particles. It is essential to evaluate the minimum steam flow rate that eliminates diffusion resistance to make the reaction chemical controlling. Encinar *et al* (2000) reported that conversion or reaction rate is independent of particle size. The effect of particle size on activation stems from the existence of a temperature gradient inside a particle. On the other hand the existence of pores could help reduce such a gradient if not eliminating it.

Bansal (1988) reported results on steam activation of pine wood at 950°C made by Caron (1985). The study demonstrated that higher char burn-off resulted in an increase in the adsorptive capacity of the final product towards nitrogen (3 – 4 Å), benzene (5 – 6 Å), methylene blue (8 – 9 Å) and molasses (12 – 20 Å). Increase in burn-off resulted in further pore widening giving a maximum adsorption capacity beyond which the wall of the pores started to collapse resulting in a decrease in adsorptive potential of the final carbon as shown in Figure 4-3.

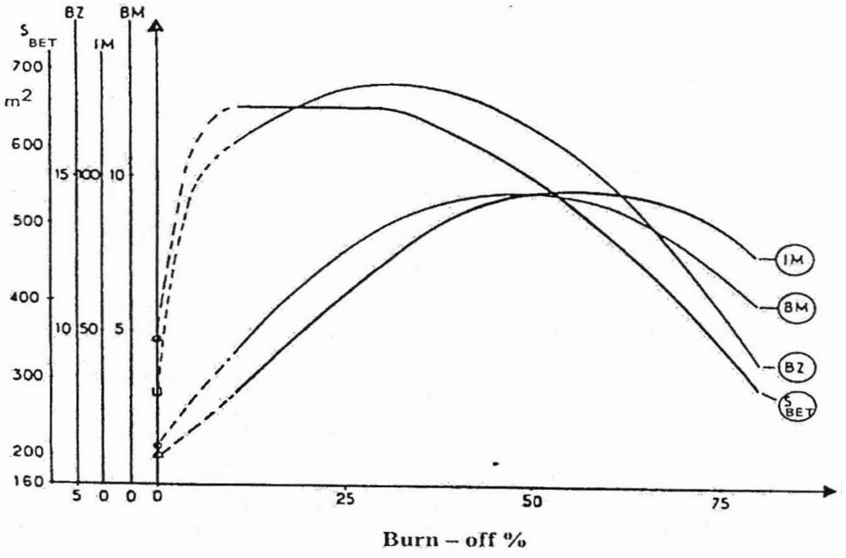

Figure 4-3 Adsorption potential of activated carbon produced from pine wood char activated at 950°C at different burn-off %. (S_{BET} = surface area; BZ = Benzene; BM = Methylene Blue index; IM = Molasses index) (Bansal, 1988)

The results clearly show how the initial phase in steam activation is dominated by microporosity development as evidenced by high BET surface area and benzene index. The later stage involved pore widening resulting in decrease in microporosity and increase in mesoporosity as indicated by the methylene blue index and the molasses index. The results confirm that the adsorptive potential of activated carbon can be adjusted according to application by varying the extent of burn-off.

4.4.4. Porosity development during physical activation

The porous texture of an activated carbon is mainly determined by precursor used, activation mechanism used, activating gas and preparation conditions (Wigmans, 1989; Manocha, 2002). Activation with CO_2 develops micropores over the entire range of burn-off while steam results in a well developed porous system with size distribution.

According to Wigmans (1989), oxygen rich feedstocks like bagasse show a narrower pore size distribution than oxygen-poor feedstock. This being the case then it should be possible to make bagasse-based active carbons of near pore size distribution for specific applications from biomass.

Porosity development is affected by the type of activating agent. The differences in activating agents in terms of reactivity, molecular dimensions combined with diffusion rate reduces the diameter of the effectively accessible pores in the order $O_2 - CO_2 - H_2O$ (Wigmans, 1989). This means steam is expected to give a well developed microporous structure. Ribes-Perez (1995) reported that steam activation produced good porosity development but the development of wider porosity agrees with the absence of molecular and Knudsen diffusion limitations. Hence porosity development is independent of the partial pressure of steam implying that the wide porosity development in active carbons is a result of the total number of active sites of the carbon formed during pyrolysis.

Carbon atoms localized at edges and periphery of aromatic sheets or those located at defect position, dislocations and discontinuities are associated with unpaired electrons or residual valencies implying high potential energy and hence these carbon atoms are more reactive and have a tendency to form surface oxygen complexes during oxidative activation. (Patrick 1995). Formation of the oxygen complexes results in selective reactivity, enhancing pore widening during activation. According to Wigmans (1989) a certain degree of oxygen functionality is essential for optimum pore structure development. The presence of C-O complexes destabilizes the adjacent free carbon active sites and the desoption of product leads to the formation of highly reactive through transient 'nascent' active sites – heterogeneity effect (Illan-Gomez *et al* 1996).

If one assumes that C-CO_2 and C-H_2O reactions pass through formation and further decomposition of oxygen surface groups on the active centers of carbon (Laurendeau, 1978), the stability of the oxygen surface groups could determine if there is pore widening or creation of new porosity. Lizzio *et al* (1990) divided surface complexes into two groups, C-O and C (O). The C-O spectator accumulates on the surface during reactions (temporary inhibitor) because their turnover is much inferior to the average turnover frequency. The C (O) complexes are true reaction intermediates because their residence time on the surface is much shorter. Thermally stable surface complexes could block reaction centers and force reactions to occur on the other regions of the carbon structure resulting in increased microporosity. Less stable oxygen surface groups decompose with ease and there will be new active sites in the internal porosity for the attack by the activating agents resulting in pore widening.

4.5. Equipment for making activated carbon

The production of activated carbon is mainly based on kiln technology. Drying of raw material, carbonization, activation, regeneration and reactivation processes all take place in kilns. There are three groups of kilns available: (1) rotary kiln type, (2) fluidized bed type and (3) the moving shaft type. The choice of a kiln basically depends on application among a number of factors discussed in this section.

4.5.1. Rotary kilns

Perry (1997) described a rotary kiln as a long and narrow cylinder inclined 2 to 5° to the horizontal, rotated at 0.25 to 5 rpm and with a length to diameter ratio ranging from 10 to 35 depending on the reaction time needed. The solids flow pattern approaches a plug flow axially and complete mixing laterally. Rotary kilns are well suited for carbonization of heterogeneous materials like biomass (Klose & Weist, 1997). The yield and product properties can be varied to a large extent by changing the process parameters in the kiln. Solids retention time in the kiln is an important design factor and is set by proper selection of the diameter, length, speed, slope and internals design. There are two basic types of rotary kilns; direct fired and indirect fired. Rotary kilns can operate in either the co-current mode where the gases and solids move in the same direction or in the counter-current mode where they move in opposite directions. Generally the material is sized after activation.

4.5.2. Fluidized bed

This is a vertical, stationary furnace in which the carbonized material is activated in a bed fluidized by the mixture of heating gases and steam. In the process, the pieces of carbonized material are pre-screened to uniform size (0.8 – 1.0g) and activated at about 1115°C. As the charcoal loses weight, it rises to the top of the kiln thus the kiln can be set so that at certain weight loss (e.g. 60%) the pieces of carbon will be driven out the top of the kiln and trapped.

4.5.3. Moving shaft oven

This is a vertical stationary furnace consisting of a number of ovens containing grates or crucibles. The carbon moves down the kiln, through each oven by gravity. Examples of kilns in this group are multiple hearth kilns and shaft ovens.

In the multiple hearth kilns, the carbon is moved spirally by rabble arms and teeth and is heated directly with combustion gas products generated by burners installed in the lower hearths. Carbon is introduced at the top and the particles fall from the top to the bottom through staggered drop holes on each oven. The raw material is dried and carbonized in the initial ovens (one hour retention time) then activated in the remaining ovens (three hour retention time). No narrow pre-screening of raw material is required.

Shaft ovens consists of narrow shafts, 10 – 20m high formed of special roof shaped bricks, containing thin outlets at the bottom of each shaft. When these are opened, the carbon is allowed to fall through. The rate of opening of the outlets governs the rate of throughput. It is not the carbon that changes ovens but the ovens are cycled through stages, that is, combustion gases from the activation stage are burnt in the combustion chamber and the hot exhaust gases pass from the activation stage are burnt in the combustion chamber and the hot exhaust gases pass through a shaft oven filled with raw material. The oven is in the 'pre-heater stage'. On reaching activation temperature, the shaft oven is converted into an 'activation stage' in which preheated steam is passed downwards through the oven to activate the carbon. The gaseous products (CO and H2) pass to the combustion chamber to heat an oven.

Table 4-7 Advantages and Disadvantages of common kilns (Rogans, 1986)

	Advantages	Disadvantages
Rotary kilns	• Low initial costs • High capacity • High quality activated carbon can be obtained	• Long activation period (24 hours) • Excessive motion of the material treated causing loss by erosion • Moving parts means high maintenance • High fuel costs or energy costs • Handling of product required during manufacture
Shaft ovens	• Energetically self sufficient • High throughput	• High initial costs • Non uniform activation occurs due to the irregularities of downward movement of materials.
Fluidized bed	• A uniform temperature can be maintained and measured accurately, resulting in a high quality carbon with a uniformity of activation • PAC or finely ground material may be processed, thus cheap carbon can be processed using this type of kiln • No handling of product is required during manufacture • Fuel costs are low (as compared to rotary kiln) • No moving parts means low maintenance • Short activation periods (4hr) and hence high throughputs.	• Standardization of kiln to a particular raw material is required and once built it cannot easily be changed to process another type of raw material • The higher concentration of steam in a fluidized bed (up to 80%) results in a carbon that has uneven activation through a cross section of granules

Table 4-8 Comparison of common kilns on design basis (Rogans, 1986)

	Rotary Kiln	Fluidized Bed kiln	Multiple Hearth kiln
Pre-crushing (mesh)	2 x 60	7 x 14	4 x 18
Drying (min)	-	-	15
Char feed rate (kg/hr)			44
Temperature	900	850-890	950
Steam feed rate (kg/hr)			265
Retention time (hrs)	20 - 24	4	3
Yield (%)	40 - 45		59
Product = CCl4 No. (%)	65	60	60
Bulk density (g/l)	500	500	540 - 550

The kilns were compared by using the following criteria:

1. Mass transfer efficiency – which determines how efficient steam of other gases are transferred to the particle surface.
2. Particle Residence Time Distribution (RTD) – this controls the rate of steam activation by proper selection of operating conditions: temperature, time and atmosphere. The activation time cannot be controlled properly unless the furnace provides a narrow particle RTD during activation.
3. Atmospherics control - oxygen levels must be controlled due to the exothermic reaction between oxygen and carbon.
4. Temperature control - gasification rate is dependent on particle temperature as well as the gas atmosphere. Thus a good furnace must have an accurate, flexible temperature control.

Table 4-9 Comparison of common kilns on control and operability (Rogans, 1986)

	Rotary Kiln	Fluidized Bed kiln	Multiple Hearth kiln
Mass transfer	3	1	2
Particle RTD	2	3	1
Atmospheric control	1	1	1
Temperature control	3	1	1

* * Ranking No 1 means the best.

Table 4-9 above shows that no single kiln is superior when evaluated against all criteria however proper design and operation helps reduce shortcomings. An example is the internal flight in rotary kilns which helps improve heat and mass transfer though difficult to maintain in the high temperature zones of the furnace.

The kilns were also evaluated in terms of costs in table below

1. Energy consumption – this depends on heat losses through the shell in addition to heat requirements for carbonization and activation. Fluidized bed requires substantial amounts of gas to fluidize the carbon, while the rotary kiln does not.
2. Make up carbon - to make up for carbon losses during regeneration
3. Equipment cost – this consists of cost of furnace and accessories, installation, contract and overhead engineering. This is influenced by the complexity of the design.
4. Operating labour
5. Maintenance – usually on moving parts and due to corrosion

Table 4-10 Comparison of common kilns on costs (Rogans, 1986)

	Rotary Kiln	**Fluidized Bed kiln**	**Multiple Hearth kiln**
Energy (x 10^6 J/kg AC)	13.9	18.6	13.9
Make-up carbon	12	9	7.5
Equipment cost	low	High	High
Operating (man/shift)	0.5	0.5	0.5
Maintenance (% of installed costs)	6.3	6	6

Since not one kiln can satisfy all criteria, the choice of kiln is dependent on application. Rotary kiln favours low steam concentration and long residence time.

4.6. Gas Analysis by chromatography

A GC is used for quantitative and qualitative analysis. The selection of columns and valving configurations rests upon the components available and the limitations they impose upon the overall separation. According to Thompson (1977), careful consideration of the restrictions imposed by certain components upon the overall separation process should guide the analyst upon the course of action whether to accept the situation with its limitations, solving the problem by columns or at the expense of added instrument complexity or reduced performance on other components or removal of the problematic component before injection. The fact remains that GC is not an absolute method and the results depend on accuracy of calibration. For a binary mixture,

$$\frac{n_1}{n_2} = \left(\frac{A_1}{A_2}\right)\left(\frac{F_1}{F_2}\right) = \frac{x_1}{x_2}$$

Where ni = AiFi.

The response factor (F) is defined as the proportionality constant between the number of gas moles (n) passing the detector and the peak area (A). This factor is not always constant over

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Where ni = AiFi.

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4.6.2. Energy recovery option

From an energy recovery point of view, Encinar *et al* (1997) identifies the gaseous products of biomass thermal degradation as a suitable source of energy despite the problems of separating liquid products. Distribution of bagasse pyrolysis products is shown in Table 4-11.

Table 4-11 Bagasse pyrolysis products (by mass balance).

	Temperature	Charcoal	Aqueous	Tar	Gas
Lutz *et al* (1997)	380°C	35.4	45.7	5.5	13.4
Perez & Cortez (1997)	400°C	30	45	5	20
Zandersons *et al* (1999)	500°C	23	48.6	8.1	20.3
Garcia-Perez *et al* (2002)	530°C	22	n/a	n/a	22

Garcia-Perez *et al* (2002) communicated that studies on the utilization of bio-oil for firing turbines concluded that the technical limitations observed could be overcome by optimizing the properties of the bio-oil in terms of alkali, ash content, viscosity, and heating value, and by modifying the gas turbines engines. Andrew *et al* (1994) used 1000l of bio-oil to run a 2.5MW gas turbine pilot plant.

Calculations by Zandersons *et al* (1999) showed that the potential heat of combustion in pyrogas is about 28.3 – 32.1 GJ/t of charcoal. From industrial practice, to produce a tonne of wood charcoal requires about 8.08 – 18 GJ of energy. Pyrogas and tar have a combined heat of combustion that exceeds the upper limit of the heat necessary to carbonize bagasse by 1.6 to 1.8 times (Zandersons *et al* 1999). According to Ng *et al* (2002), waste heat from pyrolysis can be used to maintain pyrolysis temperature at 700°C, and natural gas is used only to initiate the process. He quotes the NHV for the pyrogas at 11.1 – 18.5 MJ/m^3. Garcia – Perez *et al* (2002) analysed pyrogas and concluded that the average molecular weight is 38.1 – 38.5 g/mol with a gross calorific value of 6.4 – 9.8 MJ/kg.

4.7. Concluding Remarks

Bagasse promises to be one of the several agricultural residues for activated carbon production because its renewable, safe from an environmental point of view and in copious supply. Despite research on bagasse-based carbons that span almost 40 years, there is no evidence of commercial application of the patented processes. Only recently, Ng *et al* 2002 published a paper on process design and economic evaluation for the manufacture of GAC from bagasse. This demonstrates renewed interests in exploiting by-products of sugarcane milling as the sugar industry look for new perspectives and diversification options to survive the shrinking sugar market and low sugar prices. Studies by Pendyal *et al* (1999), Ahmedna *et al* (2000) and Marshall *et al* (2000) showed that bagasse-based activated carbons have similar sugar decolourising effects to coal based active carbons. Hence the need to develop appropriate technology for making bagasse-based active carbons. Currently the major drawback with exploiting bagasse for active carbons is the low yields and high costs of production especially energy. However the economics of the process could be improved by developing a process that produce excellent activated carbons, incorporates appropriate technology, recover and recycle energy and minimize environmental impacts. Research on potential energy recovery from process off gases is as important as the conditions for making excellent bagasse-based carbon and therefore combining these two spheres of research may be the hope for an economically and environmentally viable process.

EQUIPMENT

The laboratory pilot plant for this work consists of:

- a rotary drum screen
- a rotary batch kiln
- a steam generator
- gas cleaning and analysis system

5.1. Bagasse rotary screen

A rotary drum screen is used to remove the small bagasse particle sizes for reasons discussed below. The drum sieve is made out of a plastic drum cut in certain areas to accommodate 3000 microns sieves. The drum rests on a vertical support connected to a gear system which allows the operator to vary the tilt angle. The drive shaft of the drum is coupled to a motor via a reducing gearbox. The drum sieve is shown in Figure 5-1.

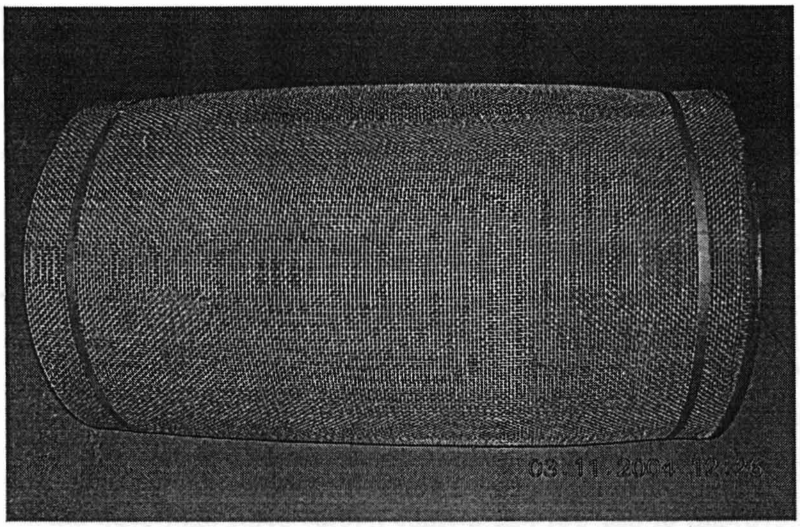

Figure 5-1Drum screen off the vertical support

A screening stage was introduced into the production process in an attempt to upgrade the value of the fibrous raw material. Bagasse is very heterogeneous and the physical and chemical behaviour of the different size fractions depends on the proportion of true fibre, rind, pith, vessel segments and non-fibrous material. Katyal *et al* (2003) reported that sieving bagasse into size fractions give samples of similar composition and hence same thermal behaviour.

According to Zandersons *et al* (1999) and Katyal *et al* (2003), finer particle sizes are heated up at a very high rate and therefore have high conversion compared to coarse material. This behaviour is a result of the difference in heat transfer limitations of the two fractions. Katyal *et al* (2003) concluded that it might be necessary to remove smaller fractions from raw bagasse before pyrolysis to reduce the amount of ash in chars. (Table 5-1).

Unlike other processes that utilize dilute acid to remove inorganic constituents (ash), bagasse screening could be a cheap and environmentally friendly alternative. Most importantly its incorporation into the production of bagasse-based activated carbon could help achieve a cost effective process.

Ash is an undesirable component in activated carbons because it does not contribute much to the adsorptive capacity and therefore is considered a diluent. Furthermore the presence of ash during the production process inhibits surface area development maybe by blocking in part or wholly some of the micropores (Valix *et al* 2004; Bernado *et al* 1997 and Pendyal *et al* 1999). As such its removal is imperative in the manufacture of high quality active carbons.

Table 5-1 Proximate analysis of bagasse fractions (Garcia-Perez *et al* 2002)

Dimensions, mm	Fractions	Volatile matter	ash	Fixed carbon
D > 4.75	34	82.3	1.3	16.4
0.85 < D < 4.75	44	82.1	1.6	16.3
0.45 < D < 0.85	15	81.8	2.3	15.9
0.25 < D< 0.45	4	72.5	13.0	14.5
D < 0.25	3	60.0	27.7	12.3

Table 5-2 by Zandersons *et al* (1999) and Katyal *et al* (2003) reported the properties of bagasse chars from different bagasse size fractions. The results confirm the undesirable qualities of bagasse fines for activated carbon production. Bagasse chars for activated carbon production should have high fixed carbon content and low ash to improve the quality and the quantity of the active carbon.

Table 5-2 Proximate Analysis of charcoal fractions (Zandersons et al 1999)

	Bagasse size fractions		
	10 >D > 1 mm	**0.5 >D > 0.25 mm**	**D< 0.25 mm**
Moisture – 2	2.0	1.7	1.6
Ash – 1	12.0	35.9	51.4
Volatiles – 1	15.1	12.2	9.7
f. carbon – 1	72.9	51.9	38.9

NB. 1 - % dry wt basis, 2 - % wet wt basis.

Other reasons for introducing the screening stage were sourced from literature:

- Chen and Chou (1993) showed that bagasse could be improved to match fibre characteristics of hardwoods by eliminating the pith (fine) fraction.
- Paturau (1969) pointed out that bagasse storage problems are caused by bagasse pith since it is attacked more quickly than fibre causing deteoration of the raw material.
- Sanjuaan *et al* (2001) reported that unbeaten pith fraction has a water retention value of 1300% based on dry substance basis compared to the fibre fraction with absorption of only 500%. This means that de-pithing could help reduce the moisture content of the bagasse feed into the drying stage. De-pithing is defined by Paturau (1969) as a combination of beating and screening of bagasse.
- Garcia-Perez *et al* (2002) reported pelletising and screening of raw bagasse as examples of methods used to reduce carryover of particles in off gases.
- The ash content has been found to be as high as 36% in bagacillo (bagasse particles<1mm) (Valix, 2001). Screening would improve the quality of the bagasse feed by reducing if not eliminating this fraction.

5.2. Steam supply system

The steam generator consists of a 6 litre container housing three heating elements. The boiler is kept slightly above atmospheric pressure by a 2.7m high pipe connected to the steam outlet of the boiler via a 630mm leg. The water feed valve (V6) for the boiler is situated at the leg such that after feeding water to the boiler, a water seal is formed in the leg. This seal offer a slight positive pressure for the boiler to enable steam to flow to the reactor. The steam flows to the reactor through copper pipes (15mm id). The lines are heated to about 110°C with nichrome wire and glass wool is wrapped around the wires for insulation purposes. Power to the nichrome wire comes via varimec and the voltage dial is adjusted to get the desired heating effect.

A condensate drain valve (V1) is situated below the rotameter to take all condensate to a bucket via rubber tube downcomer. Valve (V1) is also used to bleed excess steam when adjusting steam flow to the reactor. Valve (V2) controls the amount of steam going to the reactor. A one-way valve (V3) situated after the rotameter helps to protect the steam supply system against a build up of pressure in the kiln. Valve (V6) is available for steam calibration purposes and also to dilute steam with nitrogen (when adjusting steam partial pressures). Valve (V4) can isolate the kiln from the steam generator. Additional equipment such as a steam condenser, a water circulator and an ice water bath is connected to the steam supply system for calibration purposes. The steam supply setup is shown in Figure 5-2

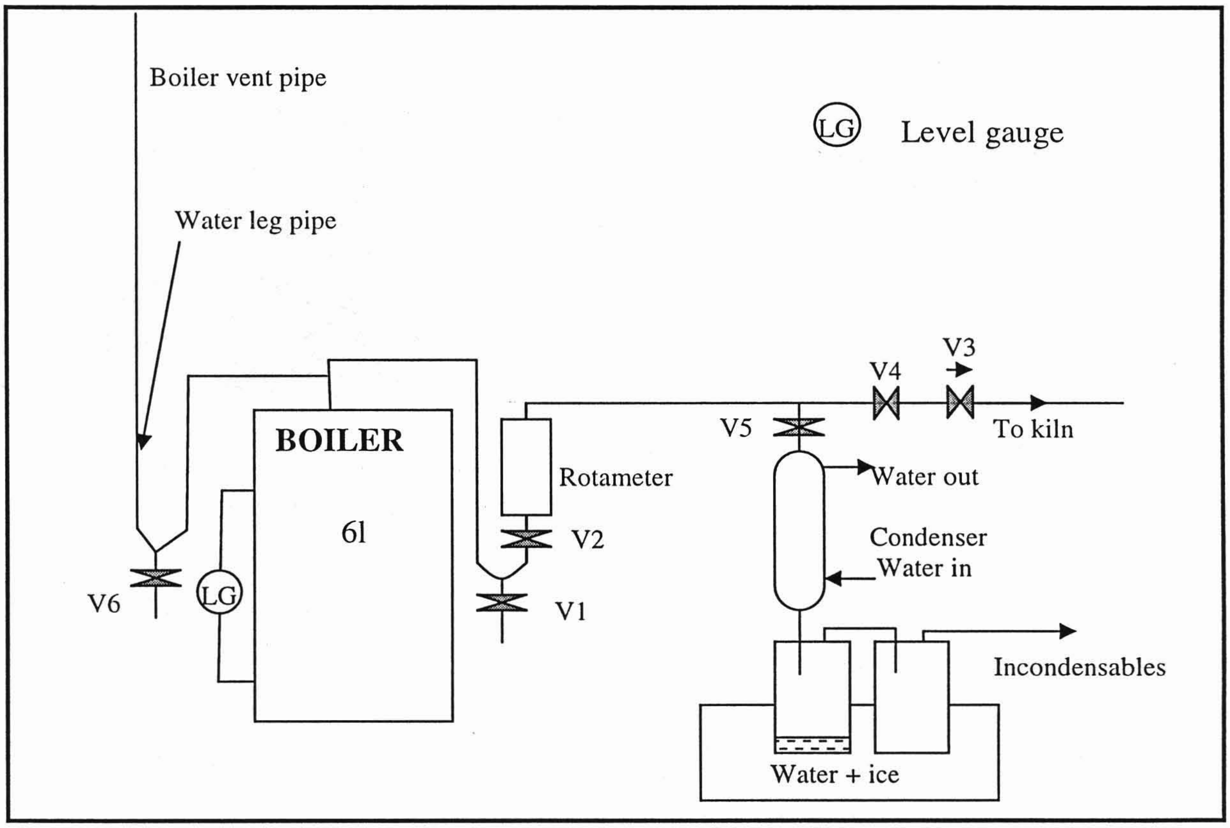

Figure 5-2 The steam supply system

5.2.1. The rotameter

After considering a number of options of how to measure the steam flowrate to the reactor, the rotameter proved to be a cheaper and accurate method. The rotameter is made of glass (10mm id) furnished with a ceramic type float. The rotameter is wrapped with aluminum foil to conserve radiant heat from the steam. Heavy insulation is also wrapped outside the aluminum foil leaving a small opening just enough to read the rotameter graduations. The rotameter setup is shown in Figure 5-3.

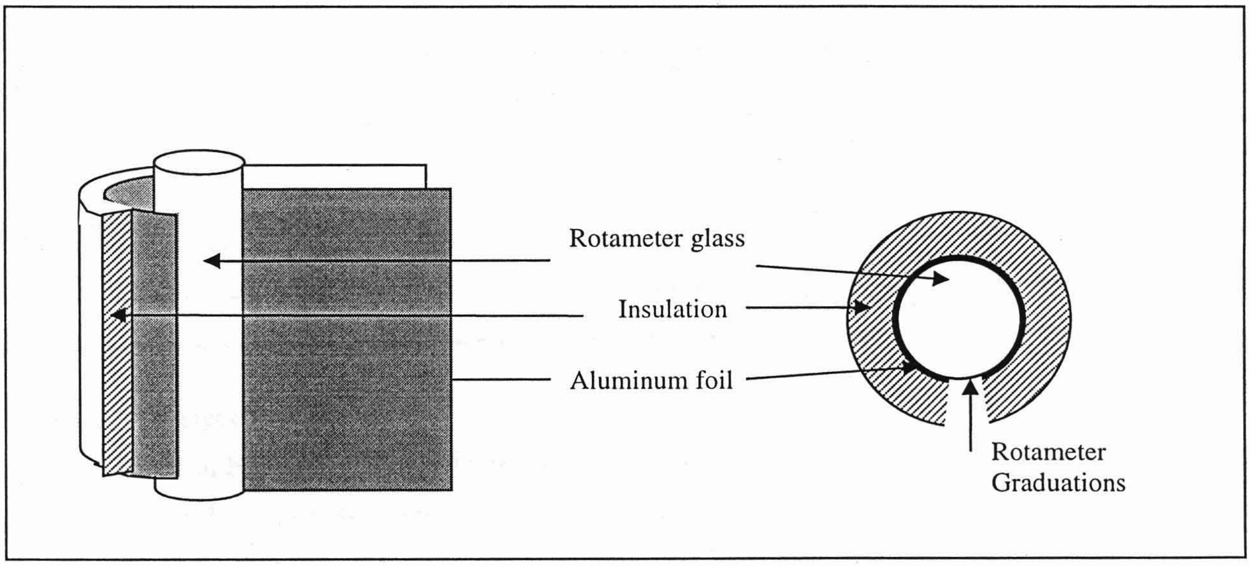

Figure 5-3The rotameter insulation

5.3. The rotary batch kiln

The batch kiln provides a quick and cost effective means of evaluating thermal treatment options. It allows use of small quantities of test material which can be very cost effective especially for expensive raw materials. The technical specifications are in Table 5-3. The kiln comprise of the electric furnace, a rotating reactor, an electric motor and a reducing gear box all sitting on a stainless steel frame pivoted to the base. The frame allows the kiln to be tilted on one end when discharging the product. The kiln is connected to a control panel which houses the main circuit breaker, the kiln drive switch, the switch for the heaters, the temperature controller model SR52 and the motor relay model FVR.C9S. The reactor temperature can go up to 1200°C according to current control configuration. As a safety measure the kiln drive does not switch off when furnace temperature is above 300°C.

Table 5-3 Technical data for the rotary batch kiln

Length	830mm
Breadth	600mm
Maximum Height	670mm
Volume of electric furnace	580mm x 340mm 180mm
Maximum diameter of the reactor	220mm od
Maximum holding capacity of the reactor	16.51
Maximum working pressure	Atmospheric pressure
Maximum Temperature	1200°C
Thermocouple	Type K
Maximum heating power	$230V_{AC}$ – 1 phase, 5KW
Mains connection	$230V_{AC}$ - 1 phase, 23A
Number of rotations	8.82 rpm (variable)
Motor	$230V_{AC}$ - 3 phase, 0.12KW
Gearbox	Type C102P, Ratio 32.8/1

5.3.1. The electric furnace

The picture in Figure 5-4 shows the inside of the electric furnace. The electric furnace comprise of an external stainless steel cover, refractory bricks at the bottom, heavy glass wool insulation (130 mm thick) on the side walls and top dambshell lid and 14 heating elements. The furnace houses the reactor and its arms freely rotate on the walls of the electric furnace. Glass wool is used to prevent metal-metal contact between the reactor arms and the walls of the furnace. The desired furnace temperature (Set Point) is set on the SR52 temperature controller. The controller shows both the SP (set point or desired furnace temperature) and the CV (control variable or the actual furnace temperature). The controller uses PID settings and the Proportional, Integral and Differential settings can be optimized manually or automatically (auto-tune) to get the desired heating rate.

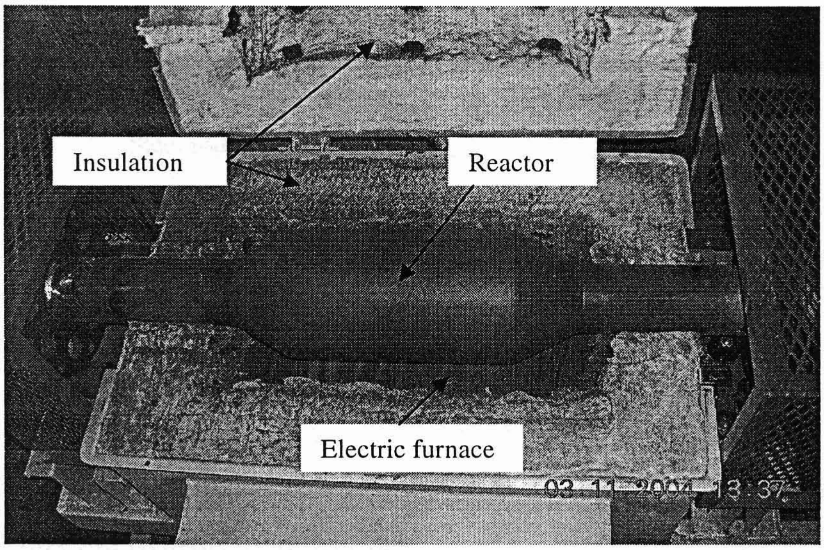

Figure 5-4 The rotary batch reactor and the electric furnace

5.3.2. The batch reactor

The reactor is a 16.5 litre stainless steel drum furnished with cylindrical arms (108mm od) one of which is coupled to a 0.12KW motor via a reducing gearbox. The reactor sits on 70 mm diameter rollers for support during rotation. The speed of rotation of the reactor can be varied (0 – 120Hz) using a control relay model FVR.095 housed in the control box. Whilst the rotating of the reactor improves heat and mass transfer of the material inside, it also leads to de-mixing through segregation of finer or denser particles (Dhanjal et al 2004) hence the inside of the reactor is furnished with flights to improve feed mixing through tumbling. Both ends of the reactor are open and provide connections for auxiliary equipment such as the steam feed pipe and gas lines.

5.3.3. Reactor modifications

The reactor initially generated a lot of sweepings (partially-pyrolysed bagasse) in the cylindrical arms during rotations prompting the addition of plates to guard the feed inside. A solid plate is fixed to the steam feed side and a retractable screen (800 microns) on the other side. The screen traps some of the airborne solid particles, allows off gases to leave the reactor and can be removed when discharging the solid product from the reactor. The modifications done to the reactor are shown in Figure 5-5. Most pyrolysis processes use nitrogen to operate under positive pressure and as a sweeping gas. This reactor utilizes the water vapour from the wet bagasse and off gases generated during the process to create a slight positive pressure in the reactor and help maintain an inert atmosphere.

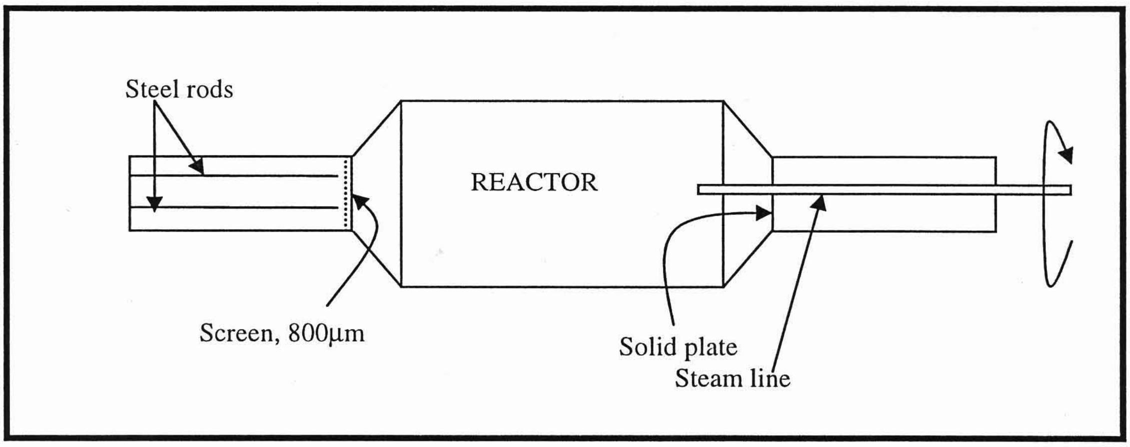

Figure 5-5 Reactor modifications.

5.4. Gas cleaning, sampling and analysis

The design of the off gas cleaning and sampling train is shown in Figure 5-6. A retractable screen situated in the kiln reduces the amount of air borne solid particles leaving the reactor with the off gases. A 90° angled rubber seal connects the off gas pipework to the rotating reactor. A 15mm id sampling probe in the off gas line takes samples to the gas cleaning system. Further purification of the off gases is done by the filter column. The off gases are cooled in the condenser (ice/water bath) and the condensate (tar + bio-oil) collects in the separator. An exit line from the separator takes all the gases (incondensable) to a silica gel column where carbon dioxide and water vapour is adsorbed. Silica gel is used to protect (and as a desiccant) molecular sieve columns, otherwise with other columns the silica gel is replaced with glass wool. Finally the gas sample is either collected in a gas storage bottle (1l) or goes straight to the GC for analysis via a two-directional GSV. The GC vents eluted components to the atmosphere. The PC records the chromatographs. The whole gas analyzing system works under a negative pressure (vacuum) which is induced by a vacuum pump connected to the venting port on the GSV via a glass ballast bottle (2l flask). The ballast helps to stabilise the pressure from the vacuum pump.

The gas sampling and analyzing equipment is divided into two main parts:

- Gas cleaning system
- Gas analysis system

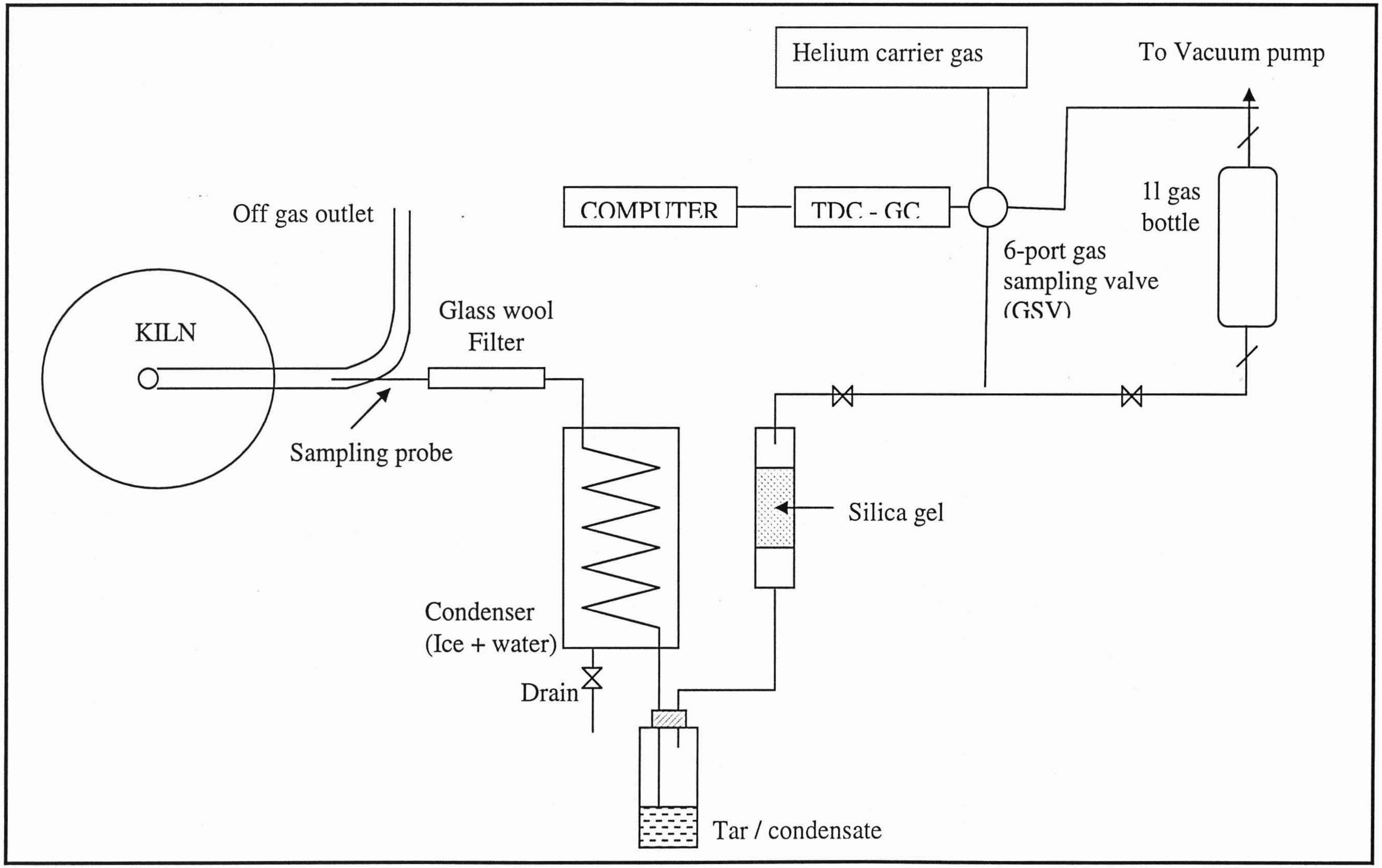

Figure 5-6 Off-gas sampling and analysis equipment

5.5. Gas cleaning system

In this work gas cleaning refers to the process of removing liquid and solid fractions from the reaction off gases to give a refined gas sample for gas chromatography. The units making up this system include filtration of solid matter, condensation of oils and tar, and adsorption of gaseous impurities. The equipment is as follows:

- 800 micron screen
- glass wool filter column
- condenser (ice/water mixture)
- dreschel bottle separator
- silica gel column

5.5.1. Glass wool filter

The particulate matter filter consists of a 50mm diameter x 150mm long column with glass wool packed inside. The column can be opened on both sides to change the glass wool. The end caps are secured with high temperature resistance rubber rings (silicon rubber) to prevent ingress of air from the surroundings. The pipework from the reactor to the filter is heated with nichrome wire and insulated with glass wool to minimize condensation of volatiles.

5.5.2. Condenser

A one pass heat exchanger type of condenser is used to cool and condense the hot off gases. The condenser consists of 15 mm id brass tubing made into a spiral in an ice/water bath of size 250 mm diameter x 400mm. A drain valve fitted at the bottom of the condenser is used to empty the water in the bath after a run. Some polythene material is used to cover the top of the ice/water bath for insulation purposes.

5.5.3. Gas liquid separator

A glass dreschel bottle 70 mm diameter x 200 mm with a rubber cork is used as a separator. Two holes are drilled onto the cork for the inlet and outlet plastic tubing. The gas-liquid mixture from the condenser is allowed to separate in the separator. The liquid collects in the separator and the gases exit to the silica gel column.

5.5.4. The silica gel column

A self indicating silica gel is filled into a 20 mm x 400mm long glass column. The purpose of the silica gel is to protect the molecular sieve column in the TCD GC from deactivation by moisture and carbon dioxide. Carbon dioxide elutes very slowly from molecular sieve compared to other light gases at low oven temperatures, hence will accumulate with time and cause a shift in the baseline of the chromatograph (Thompson, 1977). This is not desirable during gas analysis because it compromises the accurate of the results.

5.6. Gas analysis system

Gas analysis refers to the qualitative and quantitative analysis of the gaseous sample. This system involves sampling and injection of gaseous samples into the GC to give chromatographs. The equipment used in this work includes:

- 1l gas storage container
- 6-port VALCOL gas sampling valve (GSV)
- GOW MAC gas chromatography (GC)
- A vacuum pump model SPEEDVAC
- A helium (high purity) gas cylinder
- A compute integrator (PC) + interface

5.6.1. Gas bottle

A 1l glass bottle temporarily stores gas samples for later use. This enables one to use the TCD GC both online (when the reactor is running) and offline (when the reactor is not running). The bottle is furnished with air tight valves on both ends to keep samples safely inside.

5.6.2. Gas sampling valve

A two-position-six-port Valcol GSV is used for simultaneous sampling and injection of gas sample into the TCD GC.

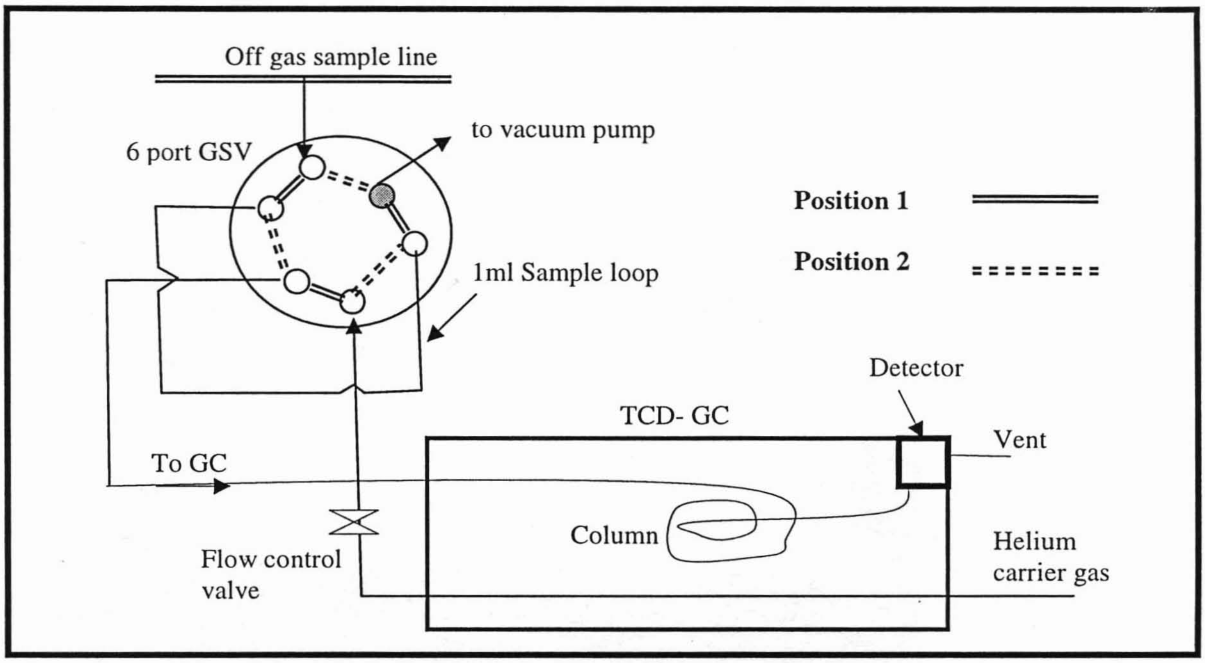

Figure 5-7 Application of two position valve GSV in gas analysis

The GSV can be used to sample and inject gas sample in two ways:

- One way to sample is to route the gas via the GSV in position 1. The off gas is kept running through the GSV and vented to the vacuum pump while the carrier gas goes via the GSV to the column in the GC. A gas sample is injected into the GC by shifting from position 1 to position 2. This method was pursued in this work. The diagram is shown in Figure 5-7.
- Another way is to use a 3-port valve with two inlets and one outlet connected to the sampling port of the GSV. One of the inlet ports is connected to vacuum pump and the other to the off gas line. The sample venting port on the GSV is blocked. By connecting the 3-port valve to vacuum pump when the GSV is in position 1, vacuum is induced in the 1ml sample loop. Changing the inlet on 3 port valve to the off-gas sample line allows gas to be sucked from the line into the 1ml external loop. By changing the GSV to position 2, the gas sample is displaced by the carrier gas (Helium) to the gas chromatography for analysis.

5.6.3. The TCD GC

A TCD-GC model GOW MAC 150 series was used in this work. The TCD-GC is connected to a computer integrator via an interface. The operating temperature (oven temperature) for separation of gases is in the range 40 - 90°C and the detector current can be varied from 0 - 170mA. Helium gas is used as the carrier gas and the pressure from the gas cylinder is regulated at a pressure of about 400kPa and a flowrate of 30ml/min. The TCD-GC is equipped with controls for carrier gas flowrate, oven heaters and temperature, detector current, attenuation, plot zeroing and polarity. The equipment is shown in Figure 5-8

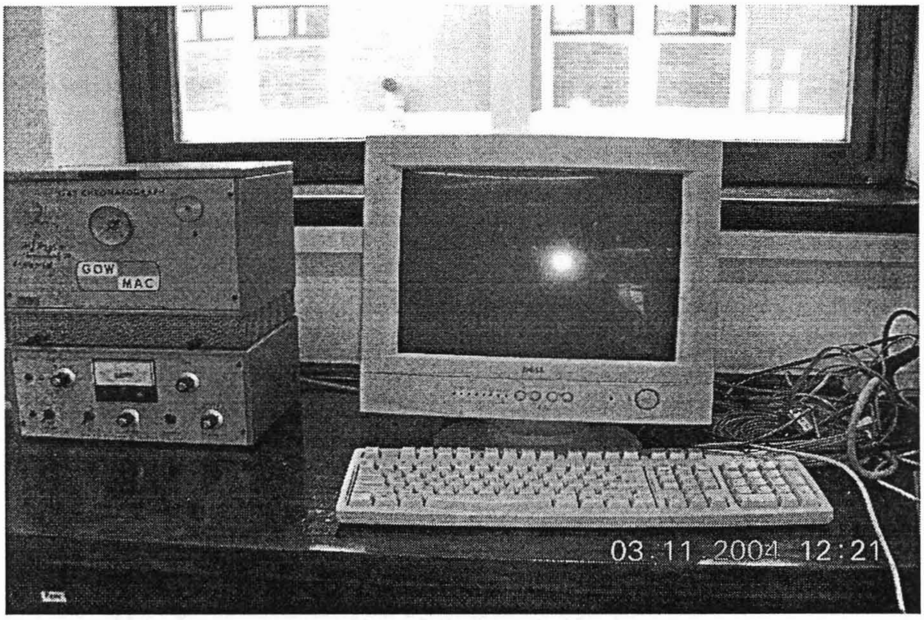

Figure 5-8 Gas analysis equipment

Two columns were used for gas analysis, namely Molecular Sieve 5A and Poropak Q. The separation technique is called Gas-Solid Chromatography (GSC).

5.6.4. Poropak Q column

The column is made from porous polymer (mostly of the bead type) and has low to moderate polarity. This column can be conditioned at about 20°C below the maximum recommended temperature (250°C) for 2 – 3 hours with normal carrier gas flow. The absolute retention times of gases using an 1829 mm x 3 mm column at 80°C; He flow rate 30cm^3/min are shown in Table 5-4.

5.6.3. The TCD GC

A TCD-GC model GOW MAC 150 series was used in this work. The TCD-GC is connected to a computer integrator via an interface. The operating temperature (oven temperature) for separation of gases is in the range 40 - 90°C and the detector current can be varied from 0 - 170mA. Helium gas is used as the carrier gas and the pressure from the gas cylinder is regulated at a pressure of about 400kPa and a flowrate of 30ml/min. The TCD-GC is equipped with controls for carrier gas flowrate, oven heaters and temperature, detector current, attenuation, plot zeroing and polarity. The equipment is shown in Figure 5-8

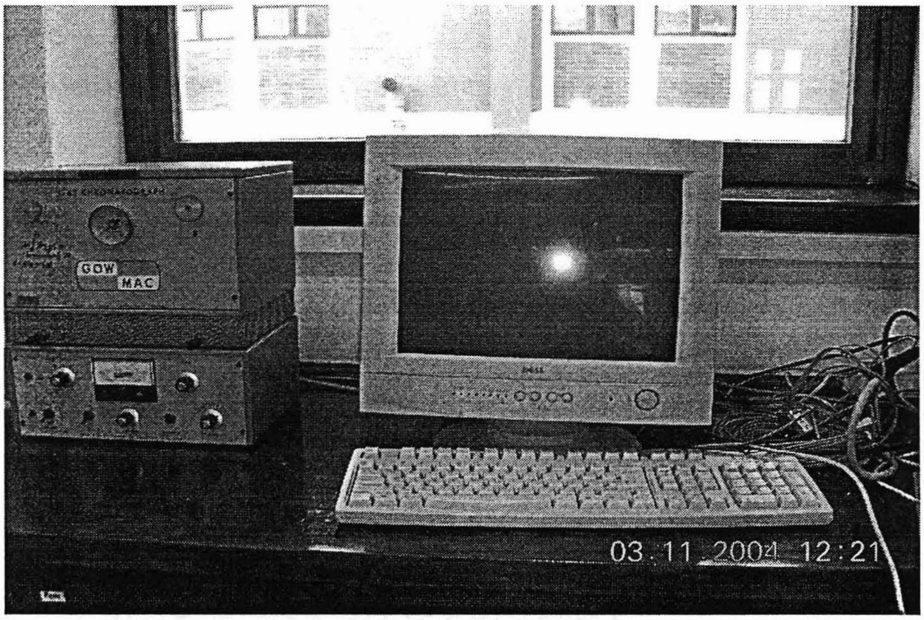

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Table 5-4 Absolute retention of gases on Poropak Q (Thompson, 1977)

Gas	Air	CH4	CO2	C2H6	C2H4	C2H2	C3H8	C3H6	SO2	H2O
Time/min	0.39	0.50	0.70	1.28	1.05	0.99	3.95	3.52	3.60	1.60^t

^{t} = tailing peak.

5.6.5. Molecular sieve 5A column

Separation of molecules in molecular sieves is basically a sieving process and elution is in the order of increasing molecular size though there are exceptions like long and thin chains. The pore sizes for MS 5A are 5Å. This column can separate hydrogen, oxygen, nitrogen, carbon monoxide and methane as shown in Figure 5-9. It strongly retains carbon dioxide but adsorption is reversible and the gas is eluted after about 30minutes. The presence of carbon dioxide at normal gas flow manifests into a drifting baseline. The column is also deactivated by moisture but reactivation can be done at 250°C for 24 hours or 350°C for 4h.

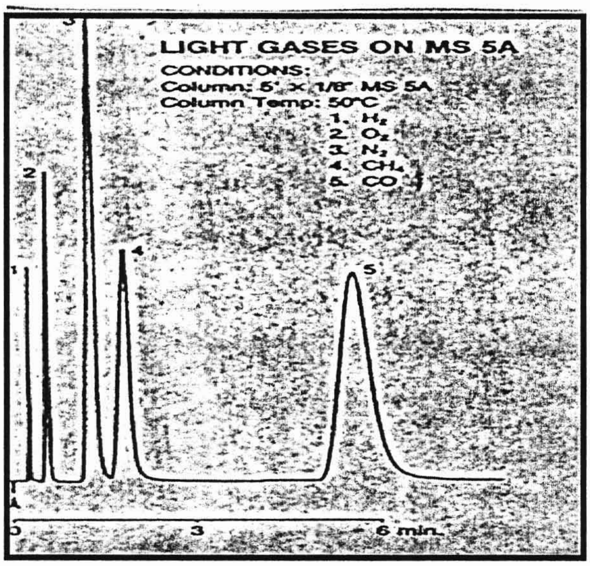

Figure 5-9 A typical chromatograph for light gases (Thompson, 1977)

5.6.6. Helium gas

High purity helium is chosen as the carrier gas for the TCD GC because of its high sensitivity, same sample polarity and high thermal conductivity compared to all gases except hydrogen. Table 5-5 shows relative thermal conductivity values (in comparison with air) for different gases in the temperature region 0 to 100°C. Hydrogen is detected with greatly reduced sensitivity when helium carrier is used and gives a negative response for high concentrations (> 6% by volume).

Table 5-5 Relative thermal conductivity of gases (Thompson, 1977)

Gas	
Hydrogen	45.9
Helium	36.9
Methane	8.6
Oxygen	6.6
Nitrogen	6.4
Carbon dioxide	4.2
Water	4.5
Argon	4.4
Carbon monoxide	6.2

A pressure regulator is used to keep a constant carrier gas flowrate to the column by maintaining a constant column resistance. The pressure regulator responds to down stream pressure changes by releasing gas at high flows to pressurize any low pressure volumes and shutting off flow to lower the pressure to desired levels.

EXPERIMENTAL

Suitable experiments were chosen to investigate the manufacture of bagasse from diffuser bagasse. The experiments were designed to give suitable and accurate information needed for the design and installation of a demonstration plant within a sugar mill. Results by Devnarain (2003) concluded that a two-step physical process involving pyrolysis and partial gasification was the best option and that process was adopted. A two stage process was chosen with respect to time of production, cost of equipment and material, and desired properties of the activated carbon in an effort to make a low cost adsorbent (Devnarain, 2003). The reasons for choosing physical activation in favour of chemical activation are fully discussed in Section 4.4.1. Additionally steam for activation is readily available at sugar mills. The equipment, process flow diagrams and process modifications are all discussed in Chapter 5. The picture for the laboratory pilot plant is shown in Appendix K.

6.1 Tests on raw bagasse.

Mill run (or fresh) bagasse was supplied from Sezela Mill in 25litre buckets. The bagasse was kept in a refrigerator to minimize microbiological activities and maintain its initial moisture content. Wet bagasse samples were used in an attempt to simulate an industrial-scale activated carbon manufacturing unit integrated within a sugar mill.

6.1.1 Particle size distribution

The fresh diffuser bagasse was analyzed for particle size distribution using screens. There were difficulties using mechanical sieving for the wet bagasse because it tends to mat together as discussed by Devnarain (2003). The high length to width ratios of the bagasse fibres made mechanical sieving very difficult. Hence manual sieving was employed and screens of sizes 4000, 2360, 1000 and 710 microns were used.

6.1.2 Moisture test

The moisture content of bagasse has a large influence on energy costs due to drying. A fresh bagasse sample was initially weighed and placed in an oven at a temperature of 110°C. The sample was left overnight in the oven to allow it to dry until constant weight. The wet and dry bagasse weights were used to determine the total moisture content. The moisture content was expressed as a percentage of the wet feed.

6.1.3 Bagasse screening

A rotary drum screen was used for screening bagasse. The rotary drum screen and reasons for screening bagasse are all discussed in detail in Chapter 5. Bagasse screening was done on a 'once through process'. The investigations were carried out by varying:

- The tilting angle of the drum (0 - 5°)
- The motor speed (0 – 100Hz)

The initial bagasse feed and the final size fractions (fines and course) were weighed to get their respective weights. The particle size distributions of the fractions were also investigated using manual sieving. Screens of sizes 4000, 2360, 1000 and 710 microns were used as above.

6.2 Pyrolysis experiments

After raw material preparation, the coarse bagasse fraction was pyrolysed in a rotary batch kiln. The equipment for pyrolysis and all modifications are discussed in detail in Chapter 5. Additionally experiments were also performed in a TGA. The TGA equipment is fully discussed by Devnarain (2003). The following checklist was prepared to improve kiln operation and act as a safe work procedure.

Start up:

1. feed wet bagasse into the reactor and replace screen and cover
2. switch on the main breaker on the control panel
3. set pyrolysis temperature to the desired value on the control panel
4. switch on the kiln drive to the desired speed
5. Switch on the electric furnace
6. switch on fume extracting fan

Shut down:

1. switch off the heaters after the desired hold time
2. allow the reactor to cool to about +/-100°C
3. stop the kiln drive
4. open reactor end cover and remove screen
5. remove the hooks that hold kiln to frame
6. lift the kiln into a discharge position – slanting position
7. start kiln drive and empty the kiln contents into a container
8. switch off all kiln controls + the mains breaker.

6.2.1 Determining optimum pyrolysis conditions

Bagasse was kept in a freezer to maintain its initial moisture content in an attempt to simulate a mill scenario. The intended pyrolysis plant will be situated within a sugar mill and fresh bagasse will be conveyed directly from the mill to the activated carbon manufacturing plant. All experiments were carried out at atmospheric pressure. In some runs the reactor was initially purged with nitrogen. For some runs process gaseous products were used as sweeping gas. The flow of nitrogen was controlled at 260m^3/min to avoid loss of feed material due to entrainment along with the gas. The temperature was set to the desired peak temperature and an average heating rate of 10°Cmin^{-1} was used. The reasons for using a heating rate of that magnitude are discussed in detail in Chapter 4. The effect of peak temperature was investigated at 600°C, 700°C, and 800°C. After allowing the desired hold time at peak temperature, the furnace was switched off to allow the solid product to cool down with nitrogen as a purging gas. The effect of hold time was also investigated at constant temperature for 1hr, 2hrs and 3hrs. The experimental approach in Figure 6-1 was followed.

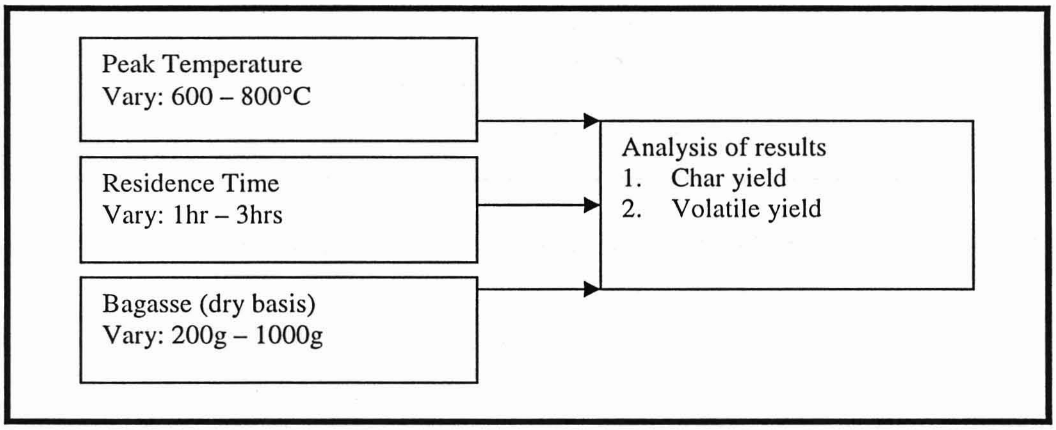

Figure 6-1 Investigating pyrolysis conditions for bagasse char in a rotary batch kiln

6.2.2 Calibrating nitrogen flow

A nitrogen cylinder was connected to a soap bubble film calibrator via a rotameter. The nitrogen gas was regulated at 200kPa. The nitrogen flowrate was varied by adjusting the control valve. The flowrate was calculated from the volume traveled by the soap bubble film in the calibrator and the corresponding time taken for the run and the results are shown in Appendix B

6.3 Activation experiments

The bagasse char was activated using steam in the rotary batch kiln. The equipment was the same as that used for pyrolysis and all process modifications are discussed in detail in Chapter 5. It is known that the final activated carbon is affected qualitatively and quantitatively by the concentration of the oxidizing agent, the activation temperature, activation time and ash content in the precursor carbon (Hassler, 1974).

6.3.1 Determining optimum conditions for activation

The char produced from pyrolysis stage was activated by partial gasification using steam. The char was subjected to varying conditions:

- Activation temperatures (800, 850, 900, and 950°C),
- Steam flowrates (0.2, 2, 5, 10, 20, 36 g/min)
- Partial pressures (34, 44, 52, 71and 100%), and
- Contact times (0.5, 1.0, 1.5 and 2 hours)
- Amount of char (22g, 33g, 110g) on dry basis

The experimental approach in Figure 6-2 was followed.

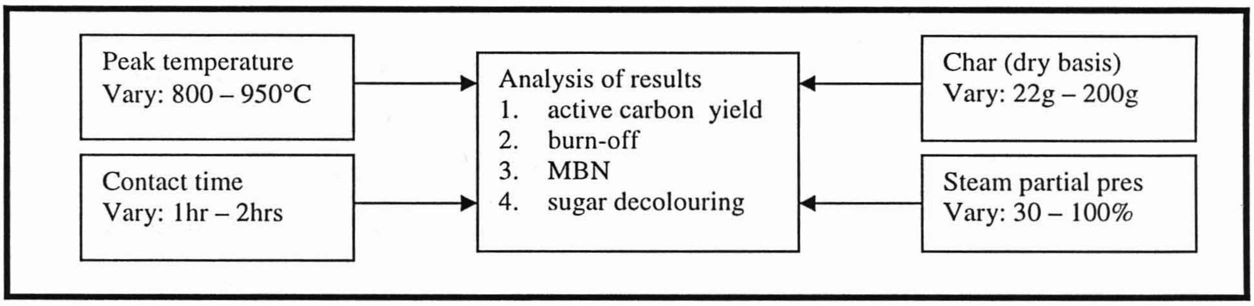

Figure 6-2 Investigating pyrolysis conditions for bagasse char in a rotary batch kiln

6.3.2 Calibrating steam flow

The water supply valve (V6) was opened to fill the boiler to about 80% and closed. The steam generating system was isolated from the reactor by closing the valve to the reactor (V4). The drain valve (V1) was kept open as a safety measure with a rubber leg leading into a bucket. Then the three heaters were switched on and took about 25 minutes to generate steam. The auxiliary valve (V5) was opened to allow steam to get to the condenser. The steam calibration setup is shown in Figure 5-2 and the results are shown in Appendix B.

The circulating-water pump was switched on to allow ice-cold water into the condenser jacket and then back into the water bath. The steam was supplied at different rotameter readings to get different steam flowrates. The flow control valve (V2) was used to set the steam flow to different rotameter readings and when the flow was not enough, V1 was adjusted. The condensate from the condenser was collected in dreschel bottles and weighed. The mass of the condensate and the corresponding time taken to finish a run were recorded to determine the steam flowrate. The steam partial pressure is calculated as follows:

Assuming ideal gas behaviour

$$P_iV = n_iRT = \frac{m_i}{M_i}RT$$

Hence, for steam,

$$P_sV = n_sRT = \frac{m_s}{M_s}RT$$

And for nitrogen,

$$P_nV = n_nRT = \frac{m_n}{M_n}RT$$

Dividing the two equations and taking $m_i = \rho_i v_i$ gives the ratio of the partial pressures,

$$\frac{P_s}{P_n} = 1.56\frac{m_s}{m_n} = 1.56\frac{\rho_s v_s}{\rho_n v_n}$$

The steam and nitrogen calibration curves are shown in Appendix B

6.4 Characterizing the solid products

The optimum conditions for the manufacture of active carbon for sugar decolourising were evaluated using characteristics such as the Methylene blue number, the yield, burn-off, and sugar decolourising isotherms.

6.4.1 The Methylene Blue Number

The MBN was evaluated using a Test Method 1.3 according to Activated carbon methods of analysis by Aktasorb Systems (Pvt) LTD. The MBN is defined as the number of milligrams of methylene blue dye adsorbed per gram of activated carbon.

A calibration curve was prepared by diluting known concentrations of Methylene blue solution with 0.25v/v acetic acid and reading the corresponding absorbance from a spectrophotometer using a light wavelength of 620nm. The calibration curve is shown in Appendix A. The calibration curve was used to determine the final concentration of the diluted filtrate using the absorbance reading. A dilution factor of 40 was used to get the actual final concentration, F. The Methylene blue number was obtained from the following expression.

$$MBN = \left(\frac{I - F}{M_C}\right) x \frac{V_s}{1000}$$

6.4.2 BPAC isotherms

A PAC's ability to remove impurities from a liquid is evaluated using laboratory scale batch treatment tests or isotherm. An isotherm is the relationship that shows the distribution of adsorbate (material adsorbed) between the adsorbed phase (that adsorbed on the surface of the adsorbent) and the solution at equilibrium. There are three recognized mathematical relationships that describe the equilibrium distribution of the solute (sugar bodies) between the dissolved (sugar solution) and adsorbed (carbon) phase. Various tests were performed by Singh (2004) at SMRI to investigate the decolourising effect of BPAC on sugar juices on a batch scale. Experiments were carried out on varying conditions of Brix (concentration of dissolved solids), contact time and carbon dosage in an attempt to get the best application procedure. The standard ICUMSA method of determining colour was used. The effectiveness of the bagasse-based active carbon was tested against commercial carbons, for example Norit PN2 and Chemviron. The experimental work is shown in Appendix D.

The percentage colour removal was determined as follows:

$$\%colour \quad removal = \left(\frac{C_b - C_s}{C_b} \right) \times 100\%$$

6.4.2.1 Freundlich isotherms

Freundlich and Heller in 1939 (Treyball, 1980) investigated the adsorption of solutions on activated carbon in their earlier studies. They developed the following empirical correlation for adsorption isotherms:

$$\frac{X}{M_c} = K_a C_e^{1/n_c}$$

This empirical correlation is widely used and assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. By plotting log (X/M_c) vs log C_e generates a straight line with a gradient = $1/n_c$ and a y-intercept = log K_a.

6.4.2.2 Langmuir isotherms

For monolayer adsorption, the Langmuir adsorption equation is expressed as:

$$q_e = \frac{QbC_e}{1 + bC_e}$$

By plotting C_e/q_e vs $1/C_e$ yields a straight line with gradient = $1/Q$ and a y-intercept = $1/Qb$. The Langmuir kinetic adsorption model considers the surface of the active carbon as an array of adsorption sites. These active sites have equal adsorption potential and each one can only adsorb one molecule giving a one molecule thick layer. At equilibrium, the rate at which the molecules are adsorbed at the solid surface equals the rate of adsorption from occupied sites.

6.4.3 Other analytical methods

Bagasse char yield calculation:

$$char - yield\% = \left(\frac{w_{ap}}{w_{rm}}\right)x100\%$$

Char burn-off calculation:

$$Burn - off\,\% = \left(\frac{w_{ap} - w_{aa}}{w_{ap}}\right)x100\%$$

Activated carbon yield calculation:

$$AC - yield\% = \left(\frac{w_{aa}}{w_{rm}}\right)x100\%$$

6.5 Flue gas Analysis

The full description of the equipment set up is available in Chapter 5. After optimizing the two-step process for the manufacture of active carbon, the gaseous products of pyrolysis (pyrogas) and activation (syngas) were analyzed using a TCD-GC. An online gas sampling valve (GSV) was chosen in preference to a gas syringe because of the problems associated with syringes. According to Thompson (1977), the sources of error in gas syringes are:

- Diffusion of atmospheric air into the syringe during transfer from sample container to GC resulting in poor precision and loss of sample integrity.
- visual setting of the plunger in the barrel is not easily repeatable process resulting in poor precision
- flow of pressurized carrier gas into syringe resulting in poor precision and sample integrity by dilution
- leakage of sample pressurized by carrier gas past the sample plunger seal resulting in poor precision and maybe loss of sample

6.5.1 Determining the amount of gaseous components

The full details of the TCD-GC setup and the GSV is available in Section 5.6. The TCD-GC set up shown in Figure 5-7 was first tested for leaks. The system was pressurized first using helium to 400kPa and then the helium supply was shut off. The pressure drop in the system was determined after 15-20 minutes. The carrier gas flowrate was adjusted to 30cm^3/min using the flow control valve on the GC and a soap bubble film calibrator. Once the flow rate was set, the temperature was set to about 60°C and the detector to about 170mA. TCD-GC was injected with air to test the column. The position of the baseline on the chromatograph was adjusted using the zeroing knob on the GC. Then pure samples of expected gaseous components were injected into determine the elution time. The light gases except carbon dioxide were separated by gas solid chromatograph (GSC) using a molecular sieve 5Å column. Carbon dioxide was analyzed separately using gas liquid chromatography (GLC) on a different column called Poropak Q. The two results were merged by comparing the methane in both results. The gases were analyzed online using 7 minutes intervals just to give enough time to allow complete sample analysis. All the chromatograms were saved in the PC.

6.5.2 Determining the response factor

There are many ways of calibrating GC for quantitative analysis. The choice of one method over others depends on application of the results, cost, urgency and desired level of accuracy. A detailed discussion on the different methods of calibration is available in Section 4.6. A one point calibration method using standard sample consisting of the required gas components was adopted. It is the least expensive and most convenient method to calibrate a GC. The response factors were calculated from the calibration curves.

6.5.3 Determining the amount of tar

The tar and aqueous solution from pyrolysis were trapped in the dreschel bottle below the condenser. The condensed liquid was evaporated at 100°C. The evaporator consisted of a water bath at 100°C. This process removes the lightest compounds, water and the residue was taken as the tar. The amount of tar was determined by finding the difference between the initial and final weight of the contents in the dreschel bottle.

RESULTS & CALCULATIONS

7.1. Raw material

7.1.1. Moisture test

A moisture test carried out on wet bagasse indicated that fresh bagasse from the mill has 49% moisture content. Devnarain (2003) reported an average moisture content of 48% using bagasse from the same mill. Moisture content in bagasse varies with operating conditions in a sugar mill such as the drying roller-mill settings, the mill cane crushing rate, *cane preparation index* and the fibre content of the cane. However for most mills the moisture varies from 46 – 52% (Paturau, 1969).

The high energy requirement for drying bagasse is a challenge for the project and hence the need to recover and recycle energy to reduce the high energy bill. The process design will reduce moisture content from 49 wt% to less than 2 wt% before pyrolysis. From literature, a drying capacity of that magnitude is only possible when drying bagasse at a temperature of about 200°C. From energy balance calculations, the heat required to dry bagasse at 200°C is about 3.0 MJ/kg of bagasse, on dry basis. This heat is enough to raise the temperature of the wet bagasse feed to 200°C and vaporize the water.

Its interesting to see how the dryer becomes an alternative source of steam from which the activated carbon plant can take steam of high energy value (200°C) compared to exhaust steam from the mill which comes at 150°C. Steam is used for activating bagasse char to make activated carbon at about 850°C.

7.1.2. Sieve analysis

Bagasse was sieved in order to determine the particle size distribution. Since the bagasse was wet and could not pass through the sieve easily, manual/hand sieving was done and the results are shown in Figure 7-1. The majority of the fibres have diameters below 710μm. The results are consistent with Devnarain (2003). The overall bagasse particle size distribution is influenced by the operating conditions within a sugar mill during cane preparation. Cane is cut down to smaller pieces by three sets of cane knives (the leveler, primary knives and secondary knives) and hammered to a fine mass of fibre in the shredders. Different settings on the milling equipment affect the final bagasse particle size distribution.

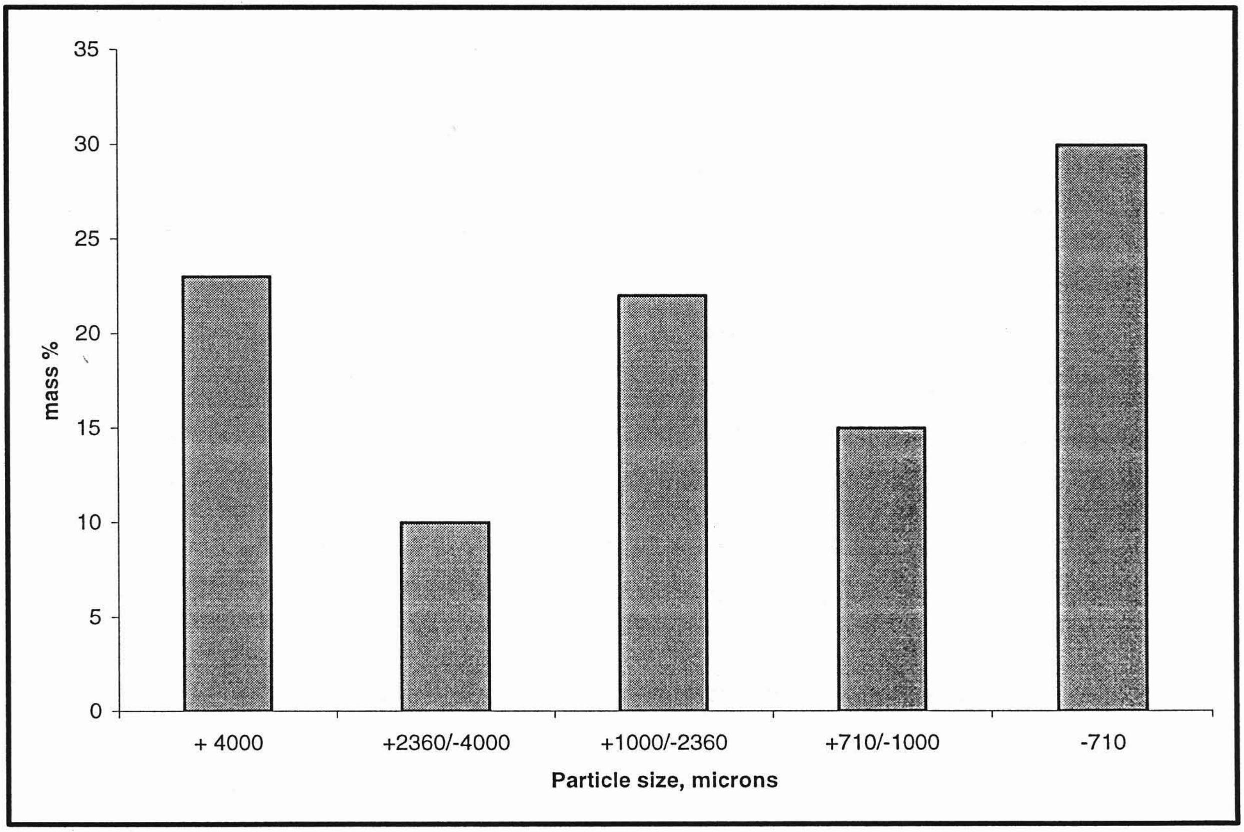

Figure 7-1 Particle size distribution of bagasse as received from Sezela Mill

7.2. Bagasse screening

The separation process was investigated on a 'once through process' by varying the tilting angle of the drum and the motor speed. A summary of the results is shown in Table 7-1.

Table 7-1 Size distribution of bagasse from the screening process

Run	Motor speed Hz	Drum speed rpm	angle θ	Hold time seconds	*Coarse fraction mass %	*Fines fraction mass %
1	12.5	4.5	5°	45	66.0	34.0
2	25	9	5°	30	61.7	38.3
3	50	18	5°	15	61.3	38.7
4	25	9	3°	30	61.7	38.3

*Percentage expressed as a fraction of bagasse feed

The drum tilting-angle θ affects the acceleration of the bagasse down the drum and hence the velocity and corresponding hold times of the material in the drum. The max tilting angle θ for the drum screen measured 5°. The results in the table show that varying the angle θ did not yield any change in the ratio of separation. It's clear from the results that the size range of the angle, 0 - 5° (for $\theta > 0°$) had no significant effect on material separation. This could be attributed to the fact that the angle is too small to impact on the dynamics of separation process.

At low motor speed (0 – 25Hz) the behaviour of the material was dominated by slow cascading movements. At high motor speed (above 25Hz) there were vigorous cascading, cataracting and tumbling movements across the cross-sectional area of the drum. Table 7-1 shows that the amount of fines separated increased with increasing motor speed and the degree of separation reaches a ceiling at higher motor speeds. This could be attributed to the changes in the dynamics of the material as motor speed increases. The vigorous cataracting movements observed at motor speeds, 25 to 50Hz, allowed effective contact between the sieve and the bagasse while low speeds allowed the wet material to roll into a mat limiting the separation of fines and sand. Motor speeds above 50Hz caused vibrations in the equipment and were not investigated. Hence a motor speed of 25Hz was adopted for the screening exercise with a screened fraction output of about 61%. Figure 7-1 shows how the rotary drum speed and the bagasse hold time varied with motor speed.

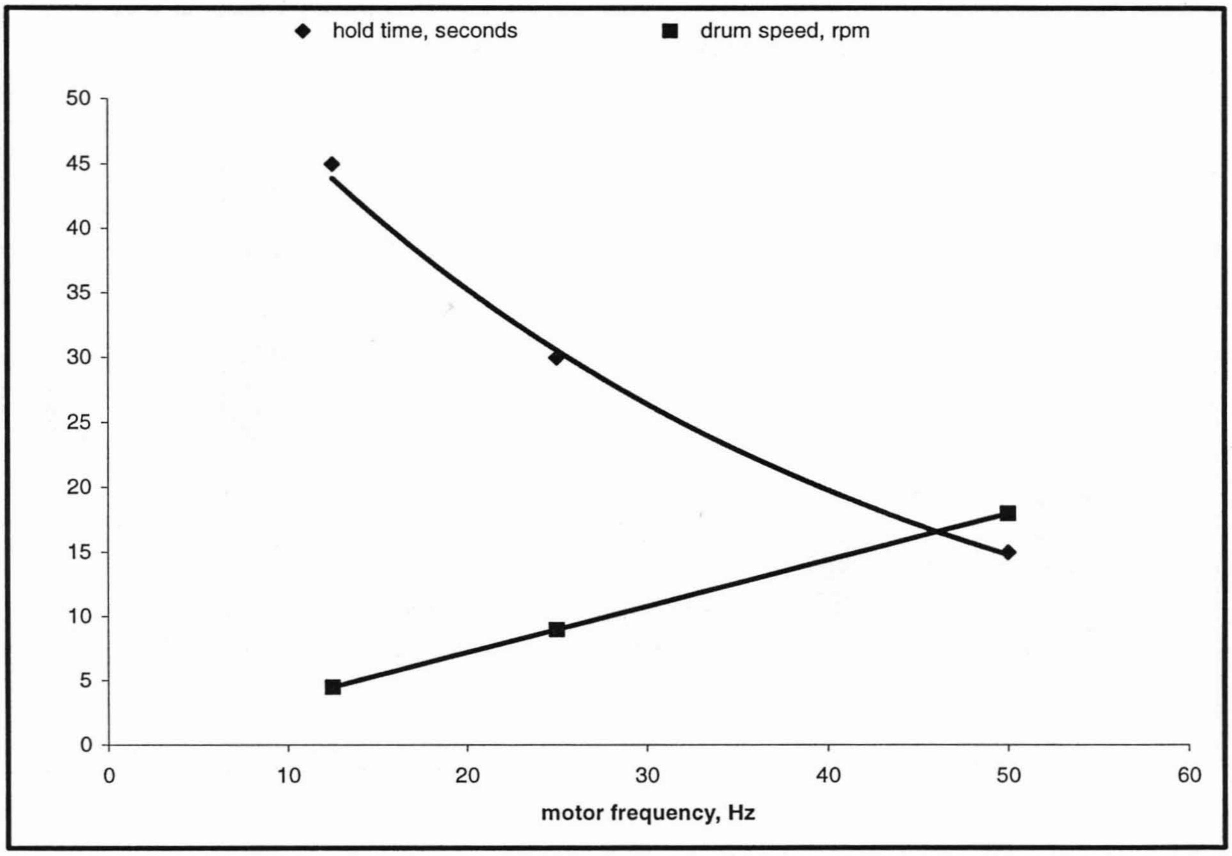

Figure 7-2 Effect of motor speed on bagasse hold-time and drum speed.

Figure 7-3 shows the effect of raw bagasse screening on particle size distribution of the final process feed. The drum screen managed to thin down the particle size distribution of the raw bagasse, increase the bagasse fraction above 4000 microns from about 25% - 60% and eliminate most of the fines (particles below 1000microns). The raw bagasse feed had about 45 wt% fines (<1000 microns) and this fraction is associated with problems of high ash content which reduces activated carbon adsorption capacity (Bernado *et al* 1997; Valix, 2001; Valix *et al* 2004 and Pendyal *et al* 1999). Valix (2001) found as high as 36% ash content in bagasse particles below 1mm. The need to screen was confirmed during initial trials when a lot of sand and ash was observed in the activated carbon samples from raw bagasse (not screened). The sand and ash diluted the adsorptive capacity of the final active carbons and caused problems with repetition of results during the MBN tests.

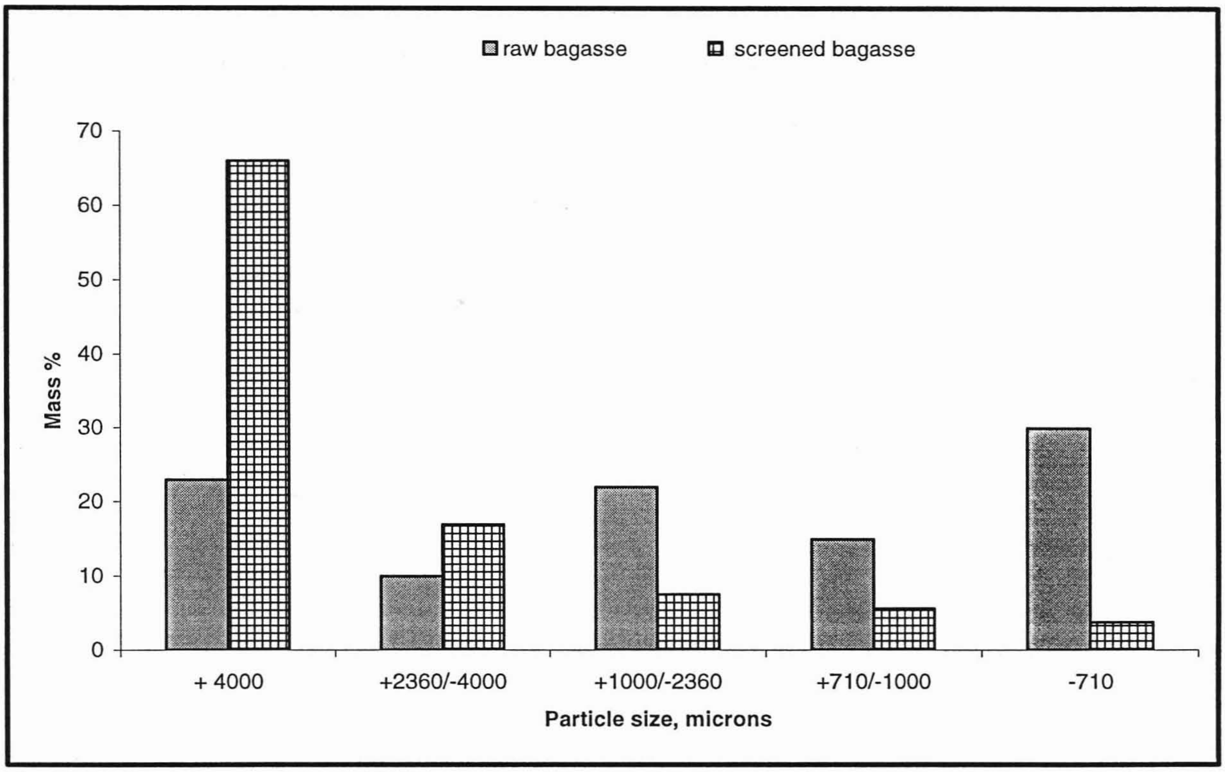

Figure 7-3 The effect of the screening process on the final bagasse particle size distribution.

7.3. Pyrolysis of bagasse

According to Bansal (1988), the final properties of the char are influenced by the pyrolysis conditions such as the heating rate, the peak temperature and the hold time. The effects of these conditions on South African bagasse were also investigated by Devnarain (2003) who used a TGA to investigate the production of BPAC from pellestised bagasse. Experiments were carried out in a rotary batch kiln to find optimum conditions for pyrolysis and also establish the scale-up effects on the pyrolysis of untreated South African bagasse. A constant heating rate of 10°C/min was used.

7.4. Pyrolysis kinetics of bagasse

The pyrolysis behaviour of the kiln was illustrated by thermogravimetric experiments. The thermogram was established by heating dry bagasse to different peak temperatures, cooling the kiln and discharging, and then weighing the mass of the final char. There was a visible colour change in the char. At temperatures of 250°C the char turned light brown and it retained its fibrous nature. It turned dark brown at 300°C above which it produced a greyish char that turned black in colour with rise in temperature.The same observations were reported by Katyal *et al*

(2003). The initial brown colour could be attributed to the volatiles coming to the surface of the bagasse during thermal degradation, then disappeared as more and more volatiles were released leaving behind the char. The colour turned black as more carbon was freed. The physical nature of bagasse changed from fibrous into a fine dispersed form. The results of the experiment are shown in Figure 7-4.

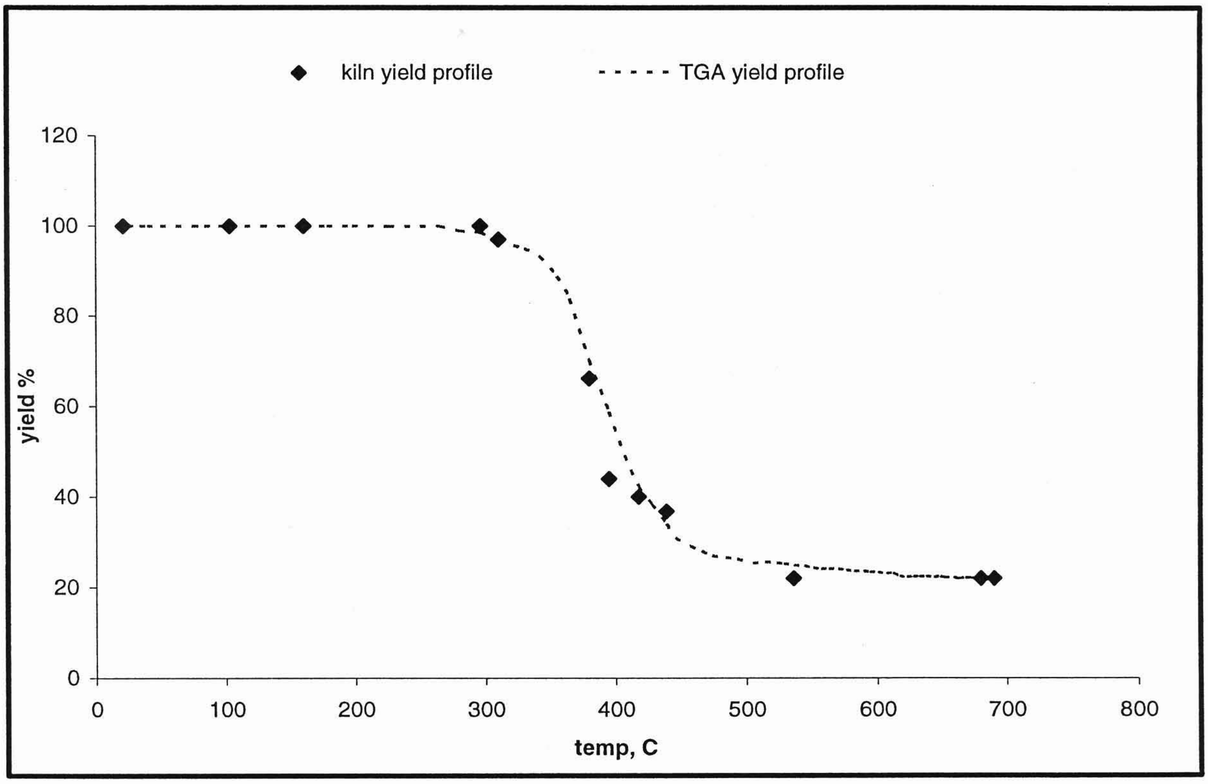

Figure 7-4 Pyrolysis thermograms of bagasse at a heating rate of 10°C/min

The two thermograms showed a similar behaviour and since a TGA is known to be more accurate, the similar results confirmed the accuracy of the manual method used to investigate the pyrolysis of bagasse in the kiln. The shape of thermograms is consistent with results by Devnarain (2003) and Garcia-Perez *et al* (2001). The results show that as temperature was increased, the yield of the char decreased with a corresponding increase in the volatiles (gas and liquid) yield. The final char yield was about 22 wt%.

The mass loss of the dried bagasse was low below 300°C at 4% compared to about 70% between 300 and 500°C. There was a small mass loss thereafter (above 500°C), about 4 wt%, confirming results from literature (Manocha, 2003) that the basic microstructure of char forms at 500°C. Pyrolysis chemistry indicates that pyrolysis starts at 100°C though the rate is small and degradation is negligible up to 200 - 250°C. This mass loss is attributed to evaporation of bound water and decomposition of polysaccharides. Between 100 and 450°C, there is degradation of extractives, hemicellulose, cellulose and lignin to give gases (CO, CO2 and H2O) and condensable liquids such as methanol, acetic acid and furfural (aqueous phase). The rate of devolatilisation peaks at 350°C and from there up to 500°C there is exothermic degradation of lignin, cellulose and extractives yielding combustible gases and condensable liquid tar. After 500°C, there is predominantly lignin decomposition with small mass loss, about 3 -4 wt% (Rodriguez *et al* 1993; Katyal *et al* 2003; Nassar, 1999; Garcia-Perez *et al* 2001).

Figure 7-5 illustrates the profiles of kiln and bed temperature, and the char yield against time. The results show that it took about 70 minutes for the kiln to heat up 700°C which translates to a heating rate of about 10°C/min. The temperature profiles show the effect of bed heat transfer limitations; the bed temperature initially lagged behind the kiln control temperature by a maximum of 200°C and the difference gradually disappears with time. This could be attributed to a high temperature differential which exceeds the bed heat transfer limitations.

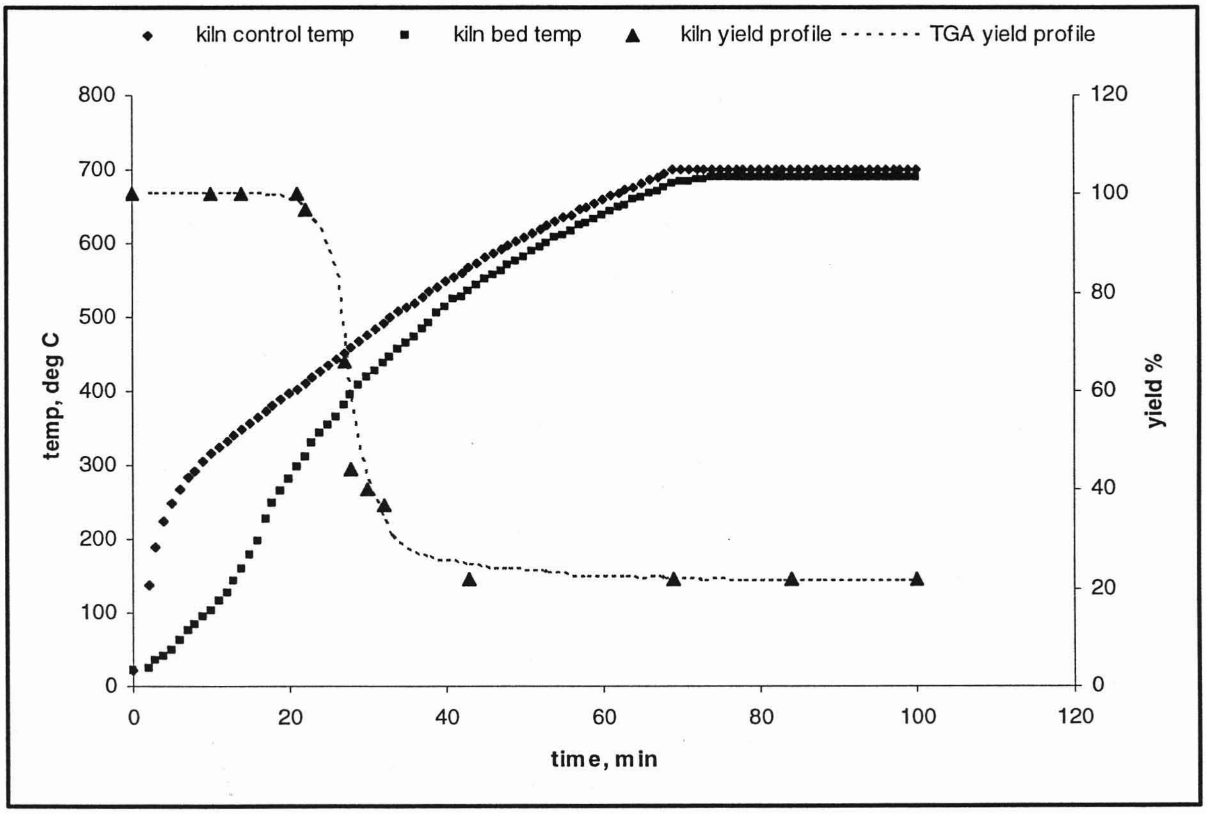

Figure 7-5 Kinetics of bagasse pyrolysis at a heating rate of 10°C/min in a rotary batch kiln

However the bed heating rate was more linear averaging 10°C/min compared to the kiln control temperature which initially jumped to a heating rate of about 30°C/min and gradually decreased with time until leveling at about 10°C/min. Mackay and Roberts (1982) reported an increase from 22 – 32% in the yield of charcoal when the heating rate was reduced from 200°C/min to 1°C/min. Both Katyal *et al* (2003) and Mackay and Roberts (1982) agree that the effect of the heating rate on lignocellulosic materials is effective at temperatures below 500°C; during the devolatilisation stage. The importance of using a low heating rate of about 10°C/min was explained by Zandersons *et al* (1999) that it promotes dehydration reactions of cellulose forming cyclic structures, and these cyclic molecules are precursors for charcoal aromatic structures.

The highest mass loss occurred in the range 20 – 30minutes, about 10 minutes before the time reported by Devnarain (2003). However both samples gave the same final char yield of about 22 wt%. This is in agreement with Patrick (1995) who reported that the degree of compaction of briquettes from straw waste from tightly bound to loosely compacted exerted no influence of the carbon yield, but only some effect on the physical properties of the carbon obtained.

Figure 7-6 shows the differential thermogram of bagasse. Only one peak was observed at about 355°C. This temperature is about 29°C less than results by Devnarain (2003) who reported 384°C. The difference between the two temperatures could be that the samples were different; Devnarain (2003) used pelletised bagasse while loose bagasse was used for this study eliminating high mass and energy transfer limitation compared to the earlier. However the single peak observed corresponds to a cellulose peak. The featureless broad, single peak for pyrolysis of bagasse is representative of samples that have not undergone pretreatment or not catalyzed (Devnarain, 2003; Antal and Varhegyi, 1995). Bagasse is a complex matrix of hemicellulose, cellulose and lignin and a hemicellulose peak is usually observed below 300°C while the lignin one appears above 400°C. Another probable reason why the other two peaks do not appear was because of vapour-liquid interactions occurring in large sample sizes compared to sample sizes used by other researchers. The differential thermogram indicates the rate of generation of volatiles (gas and liquids) by assuming that mass loss was due to thermal degradation of bagasse only. The curve shows an initial low rate of generation of volatiles at temperatures below 300°C, then the rate increased to a maximum of about 9.3 wt% /min at 355°C, after which it fell back to zero.

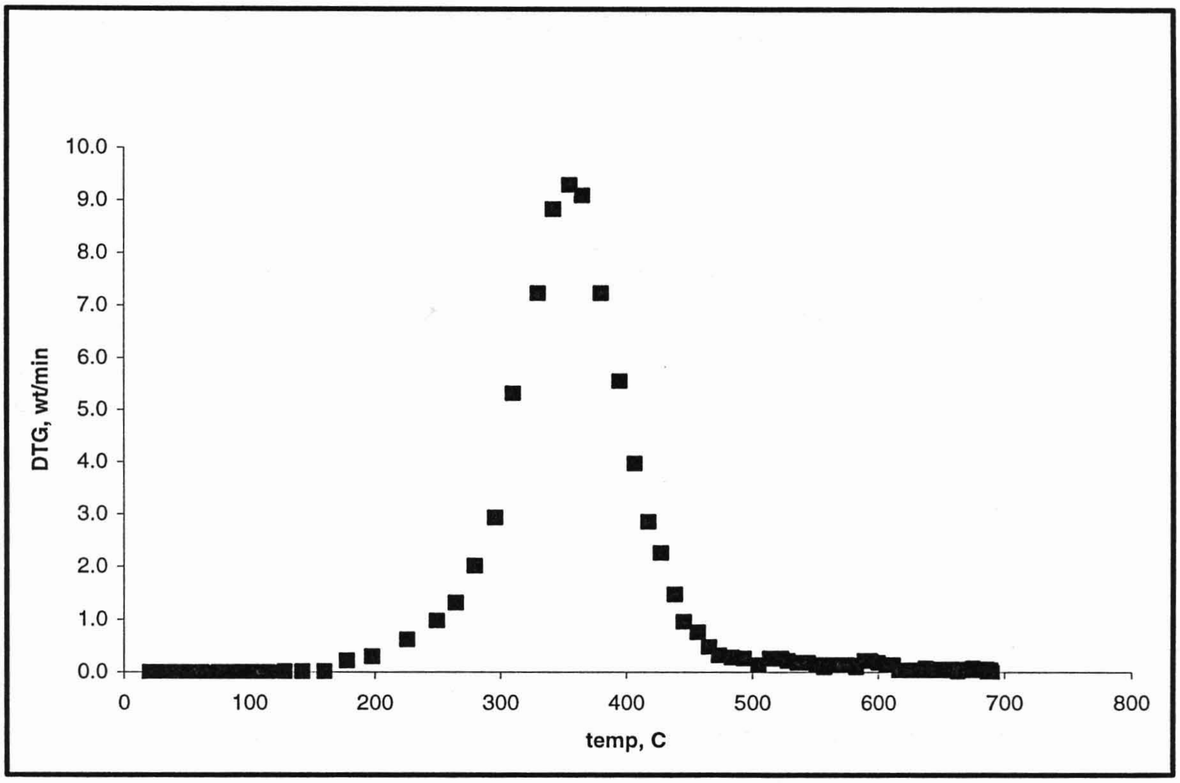

Figure 7-6 Differential thermogram of South African bagasse at a heating rate of 10°C/min

Dry bagasse (dried in an oven at 110°C to constant weight) samples of 100g from the screening process were heated to peak temperatures of 600, 700 and 800°C. Temperatures above 800°C were not considered since such treatment leads to hardening of the carbon structure due to partial alignment of the graphitic planes and a corresponding decrease in porosity which then influences the final active carbon quality (Manocha, 2003). Figure 7-7 and Figure 7-8 show the effect of peak temperature and hold time on pyrolysis of bagasse at a heating rate of 10°C/min. The results show a decrease in char yield as pyrolysis temperature was increased from 600 - 800°C and this could be attributed to the removal of lighter volatile matter first followed by bigger molecules with increase in temperature. However the char yield later approached a constant value as the volatiles released at a certain temperature finished with time. Results by Devnarain (2003) on the same bagasse showed that the Iodine number peaks at about 700°C at a char yield of 22%. A high iodine number indicates an ideal char for activation because of the high microporosity available. The above results shows char yield of about 22 wt % at a peak temperature of 700°C for a residence time of 1 hour. Many researchers also confirm 700°C as the best peak temperature when preparing char for activated carbon (Devnarain, 2003; Pendyal *et al* 1999; Minkova *et al* 2000; Xia *et al* 1998) and hence a peak temperature of 700°C and hold time of 1hour were adopted as the best conditions for pyrolysis.

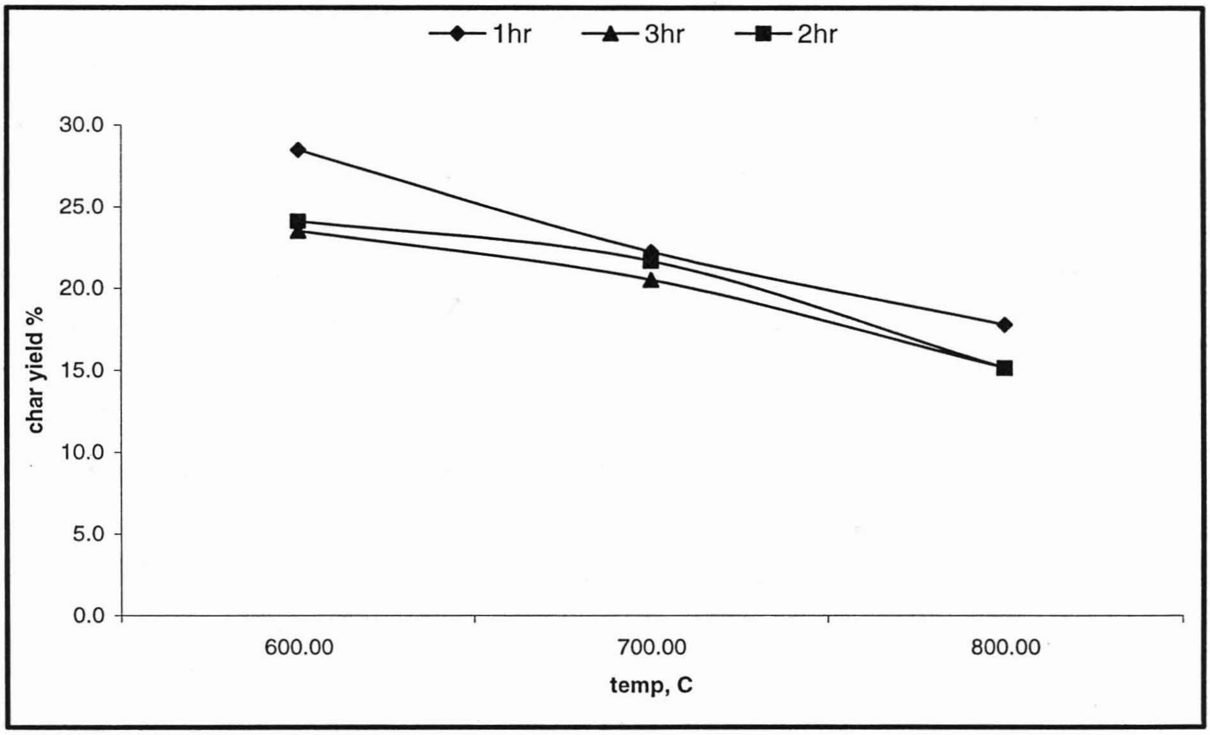

Figure 7-7 Effect of Peak temperature on bagasse pyrolysis at heating rate 10°C/min

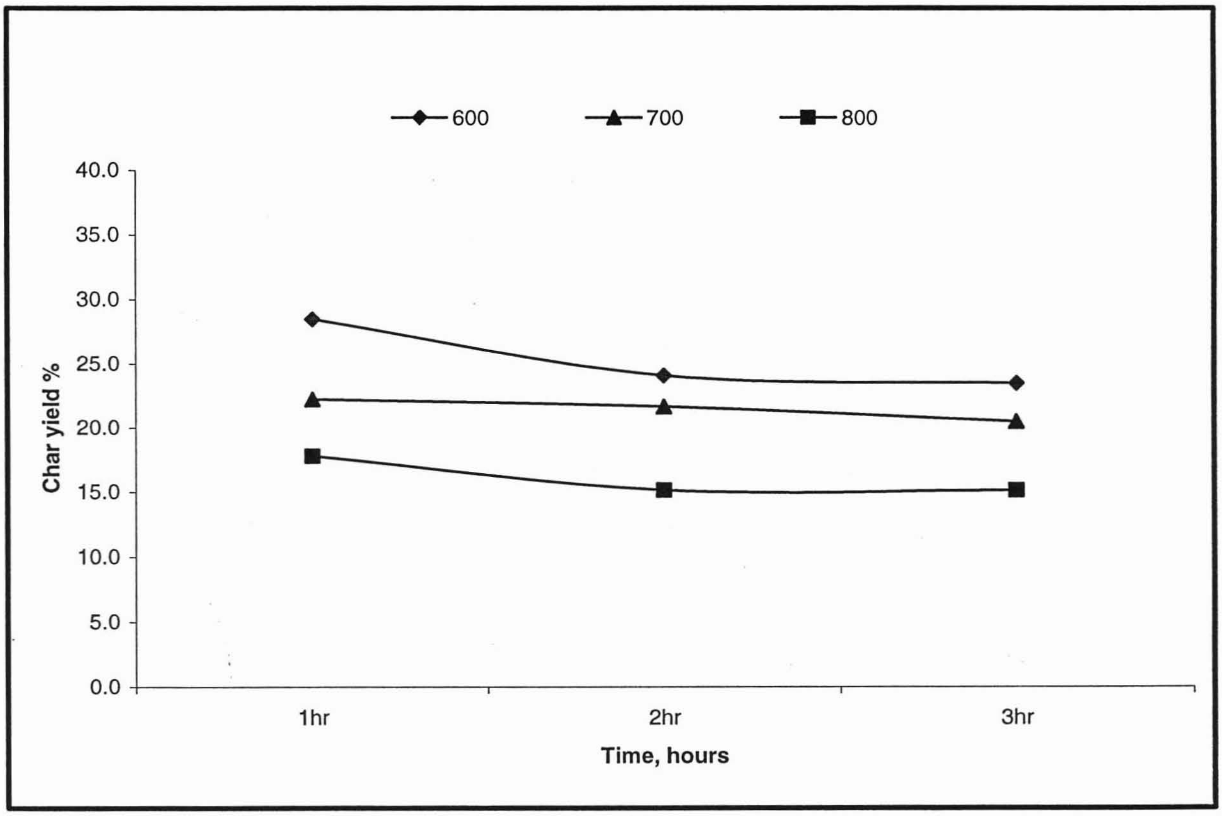

Figure 7-8 Effect of hold time on bagasse pyrolysis at a heating rate 10°C/min

7.5. Activation of bagasse chars

Bagasse was initially pyrolysed at 700°C for an hour to make bagasse char. The char was then subjected to steam activation experiments at different activation conditions of temperature, steam flows and concentration and hold time. The main purpose of activation is to enlarge the micropores to mesopores and minimize generation of macropores which are of little significance to active carbons. As discussed in Chapter 4, the quality of active carbon depends on the nature and concentration of the oxidizing agent, the activation temperature and the activation time.

7.5.1. Effect of steam flow and concentration on activation

Experiments were carried out first to establish a suitable temperature and hold time for making activated carbon by varying temperature from 850 - 950°C and activation time from 1 – 2 hours. Using an excess of steam flow at 36g/min, it was possible to get the best operating temperature and activation times for making active carbon using char of about 20g. With steam, the activation temperature must be high enough (800 - 1000°C) to provide a rapid rate of oxidation, but temperatures above 1000°C should be avoided because they reduce adsorptive powers of the active carbon (Hassler, 1974).

Table 7-2 shows that activation at 850°C for an hour produced the best results with an MBN of 92 mg/g of active carbon at a steam flow rate of 36g/min. Excessive steam flow rate can also affect the porous structure in carbons and therefore these conditions were investigated further by reducing the steam flow rate from 36g – 0.2 g/min. From the table below, there was an initial increase in MBN with decrease in steam flow rate. The best MBN generated was about 257 mg/g of carbon at a steam flow rate of 5g/min. subsequent decrease in steam flow rate from 5 – 0.2 g/min resulted in decrease in MBN. Though all steam flow rates investigated were above the stochiometric requirements of the gasification reactions, the unexpected fall in the MBN could be a result of the positioning of steam supply pipe in the reactor and other dynamic factors within the reactor. However this line of thought was not investigated further since it fell outside the scope of the project. The best activation conditions adopted for making BPAC were a steam flowrate of 5g/min at a peak temperature of 850°C for an activation time of 1hour.

Table 7-2 Determination of optimum steam flow

Steam, g/min	Temp, deg C	Time, hr	MBN, mg/g
36	850	1	92
36	850	2	73
36	900	1	62
5	850	1	257
2	850	1	180
0.2	850	1	173
5 then 0.2	850	0.5 each	207.5
5	900	1	196

After using pure steam, an investigation was carried out to see the effect of diluting the steam on the final active carbon quality and quantity. Figure 7-9 shows the effect of steam partial pressure on the active carbon yield percentage and the MBN. Initially there were linear relationships of the active carbon yield and MBN with increase in steam partial pressure up to about 80% above which the change in carbon yield and the MBN reduces significantly. Increasing steam partial pressures increase the rate of carbon gasification reaction. Given enough time all steam partial pressures would eventually give the same amount of burn-off. However this would not be feasible because plants work with production targets, hence the need for fast kinetics.

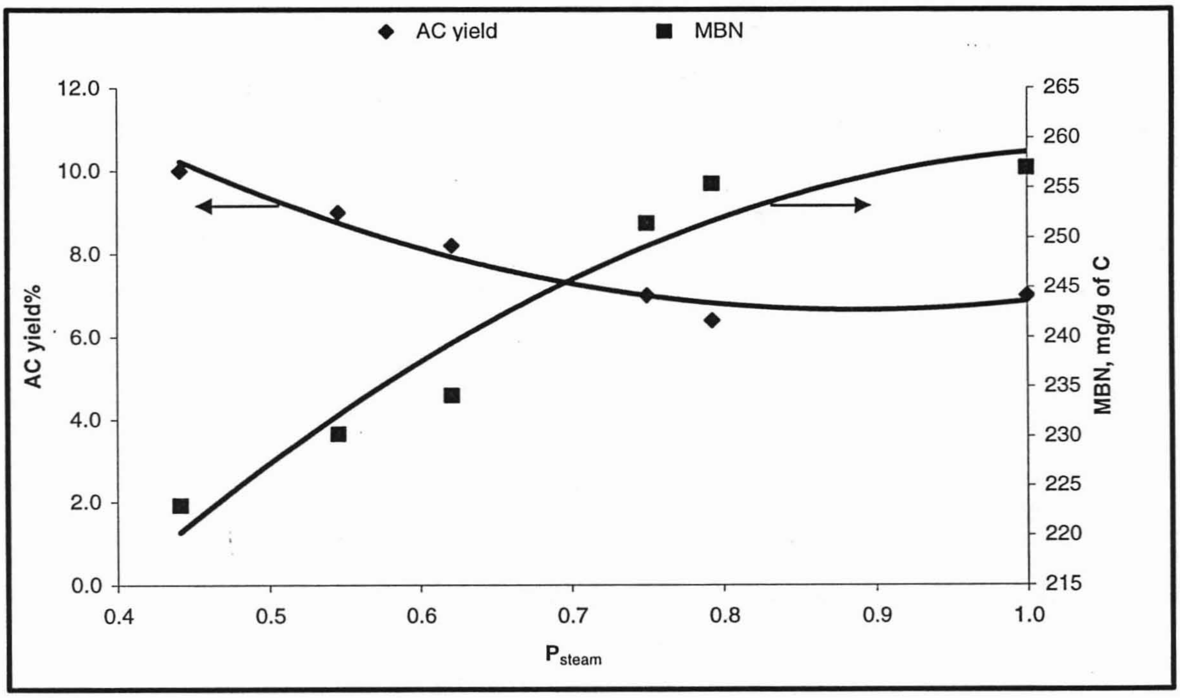

Figure 7-9 Effect of steam partial pressure on the active carbon yield and the MBN

The increase in MBN (and corresponding decrease in active carbon yield) was attributed to the increasing burn-off percentage as shown in Figure 7-10. The results show that the active carbon yield decreased linearly with increase in Burn-off. Burn-off is sometimes used to measure the degree of activation. The MBN also increased linearly with Burn-off within the limits of the investigation. The linear relationship between burn-off and surface area (similar to MBN) has bee reported in literature (Cunliffe and Williams, 1999). This was expected considering that a burn off of 50 – 75% generates mesopores (Dubnin and Zaverina, 1949) which give rise to higher adsorption of the methylene blue dye. However the surface area reaches a maximum at a limiting degree of burn-off which is specific to the initial char.

The steam-carbon reactions increase the total surface area and volume of the pores. As discussed in Chapter 4, the steam initially reacts with tarry substances trapped in pores and disorganized carbon resulting in an increase in microporosity, but further reactions (burn-off > 50%) result in the widening of pores as the steam starts to eat away carbon from pore walls. Eventually a greater amount of mesopores and macropores are generated with a corresponding reduction in the specific area of the pores. The development of mesoporosity is an important aspect of the carbon activation bearing in mind the final use of the carbon.

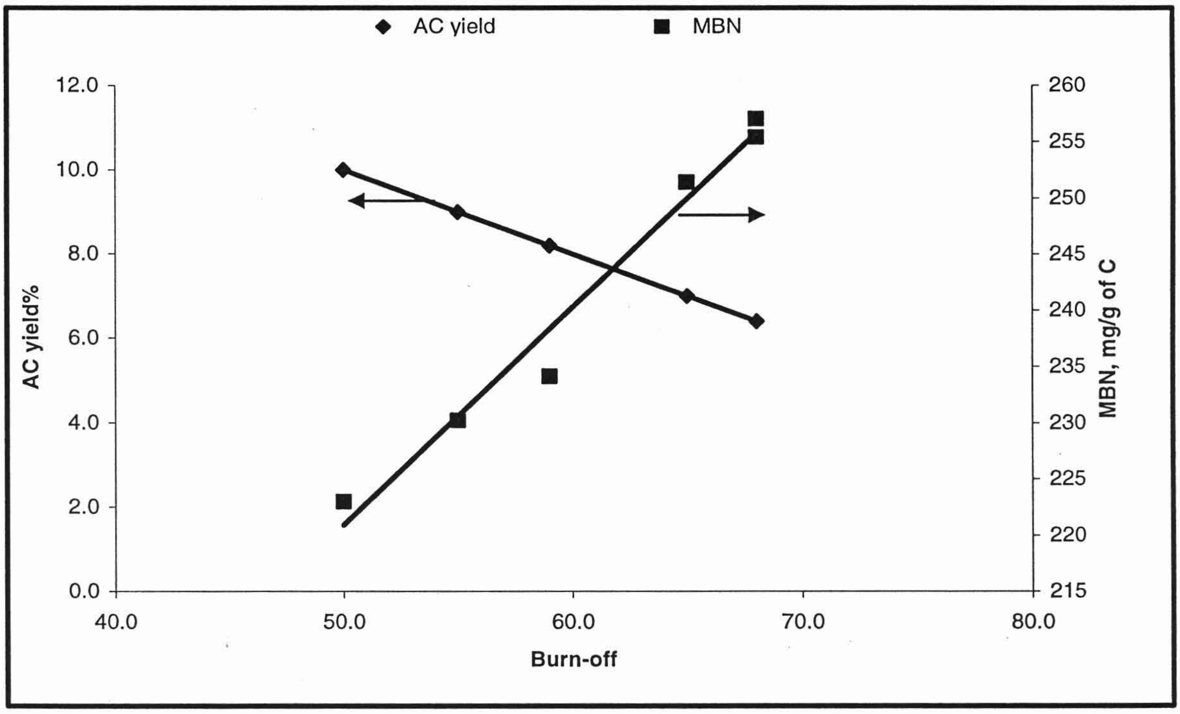

Figure 7-10 Effect of burn-off on the active carbon yield and the MBN

7.5.2. Effect of temperature and activation time on activation

7.5.2. Effect of temperature and activation time on activation

Figure 7-11 shows the effect of the activation temperature on the final active carbon yield. When 20g of char was kept at temperature of 850, 900 and 950 for 1, 1.5 and 2 hours in the presence of excess steam there was a decrease in the char yield percentage with increase in temperature. The decrease in char yield could be attributed to the increase in the char reactivity with temperature in the presence of an oxidizing agent. The higher the temperature the faster the reaction and this leads to a higher carbon burn-off in a shorter space of time. The nature of the oxygen functional groups depends strongly on the temperature for oxidation. The oxygen containing groups on the carbon surface may be basic or acidic. Oxidation above 200°C leads mostly to formation of acidic groups, which adsorbs predominantly cations. Oxidation above 500°C leads mainly to formation of oxygen groups of a basic character (Zanzi, 2001; Bansal 1989). The pH of the active carbon is an important factor in sugar decolourisation since acidic conditions tend to favour the reduction of sucrose to invert sugars (glucose and fructose). Formation of invert sugars is not desirable since it translate to loss of sugar (sucrose). The full details of the importance of pH in sugar decolourisation are discussed in Chapter 3.

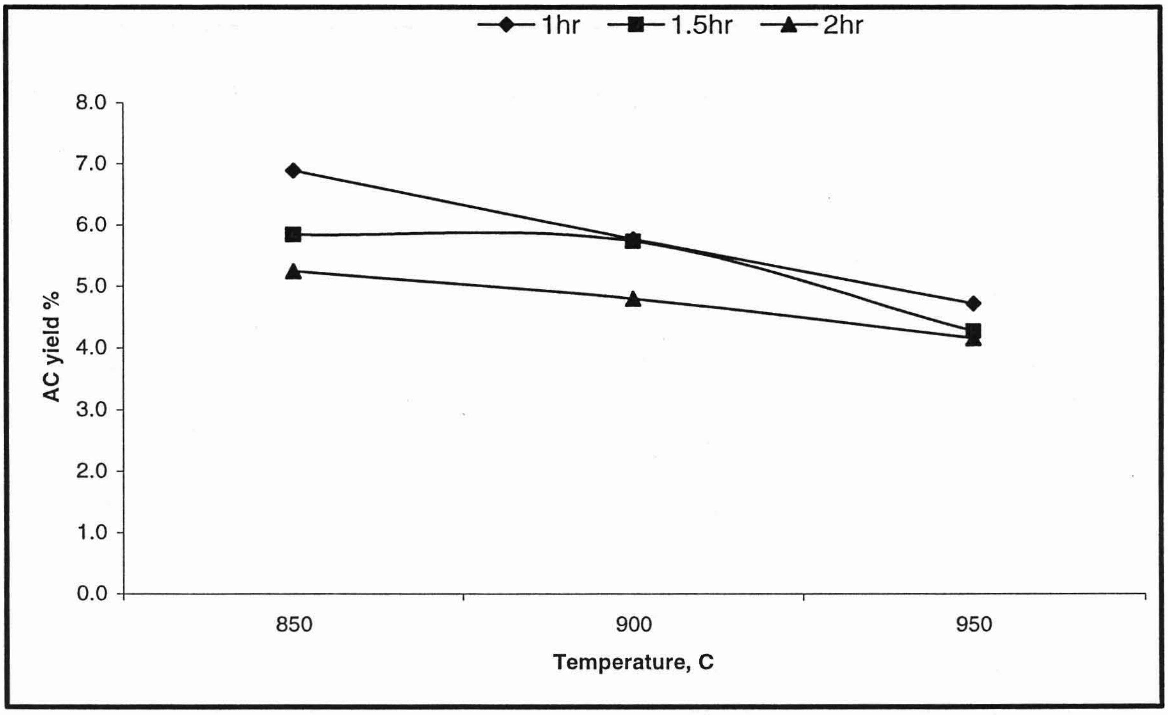

Figure 7-11 Effect of temperature on active carbon yield at constant steam flow rate of 36g/min

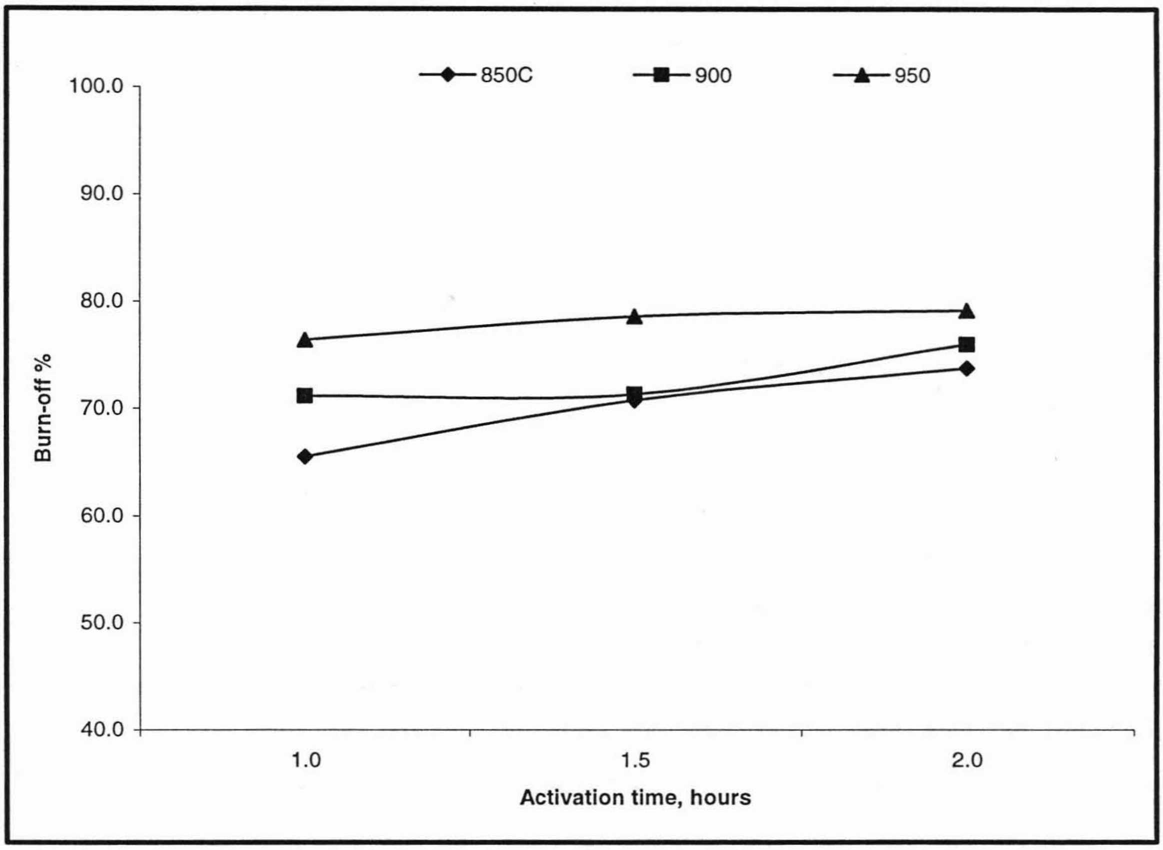

Figure 7-12 Effect of activation time on Burn-off percentage at a steam rate of 36g/min

The exposure time of char to steam is known to affect the quality of the final active carbon. The effect of activation time 1, 1.5 and 2 hours at 850°C, 900 and 950°C were investigated at a steam flow rate of 36g/min. The results are shown in Figure 7-12. Increasing the activation time resulted in increased burn-off percentage of the carbons produced. Initial mass loss up to 1.5 hours was rapid maybe because of the reactions of the steam with tarry substances coupled with the loss of disorganized carbon. The rate then falls between 1.5 and 2 hours because of the decrease in surface area of the pores with increase in pore sizes. However the times reported in this study are less than exposure times reported by Devnarain (2003) because of the difference in bagasse preparation. Devnarain (2003) used ground and pelletised bagasse samples which resulted in poor heat and mass transfer because of the tight nature of the sample. Loose char reacts with steam faster than pelletised char because of lesser pore diffusion limitations; hence loose char takes a shorter activation time to attain the same conversion (burn-off). The importance of finding an optimum activation time is also illustrated in Figure 7-13 which shows a decrease in MBN with increase in initial char feed.

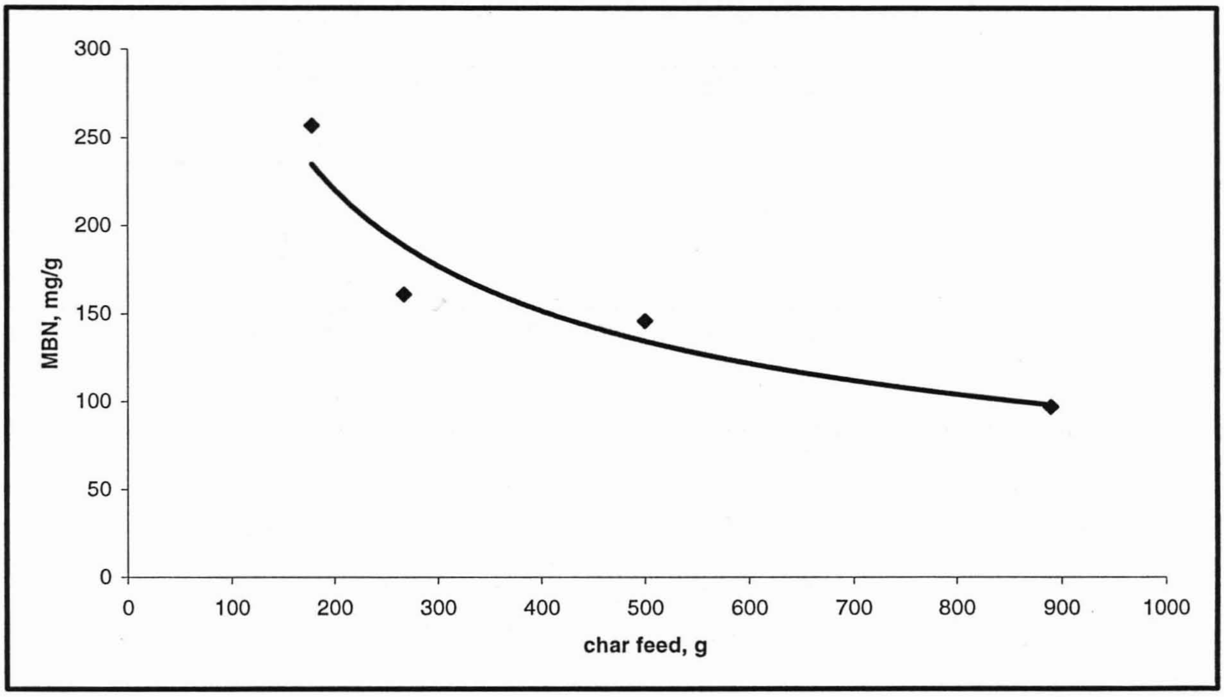

Figure 7-13 Effect of the amount of char feed on active carbon quality

7.6. Gas Analysis Results

Minimization of energy consumption from external sources is an important aspect to the success of the project and hence investigations were carried out to assess the by-products of the BPAC process and establish potential energy that could be recovered. Pyrolysis and gasification are thermochemical processes that can be directed to the preferential production of one of the three components: solid product, liquid fraction and gas.

7.6.1. Pyrolysis products

The pyrolysis of bagasse was carried to a peak temperature of 850° at a heating rate of 10°C/min and the products were trapped and separated using a gas cleaning system. The full details of the gas cleaning system are discussed in detail in Section 5.5. The system consisted of equipment for removing liquid and solid fractions from the reaction off gases to give a clean gas sample for the GC. A mass balance was carried out and the results are shown in Table 7-3. The product distribution was comparable to results published in literature by Zandersons *et al* (1999). The differences could be attributed to experimental errors especially on determining the amount tar. Some tar condensed in the filter (glass wool) and the amount was difficult to determine.

Table 7-3 Pyrolysis products from bagasse (wt %, on dry bagasse basis)

	Zandersons *et al* 1999	**Batch Pilot Plant**
Charcoal	23	22
Aqueous phase*	48	48
Tar	8.1	5
Gas	20.3	25

* Aqueous phase refers to a dilute mixture of water and soluble oils.

Further analysis of the gaseous products was carried out to investigate the energy value of the gases. The gas analysis system consisted of sampling and sample injection equipment and a TCD GC. The full details of the set up are discussed in Section 5.6. The results of the gas analysis are summarized in Table 7-4. The principal components of the gases detected were: CO, CO2, H2, CH4 and small quantities of some hydrocarbons such as ethane, ethene and propene. The results are comparable to those reported by Garcia-Perez et al (2002). The generation of the principal gases was thermal, with hydrogen from cracking of volatile matter, methane from cracking and depolymerisation reactions, and oxides of carbon from decarboxylation and depolymerisation (Shafizadeh, 1968). However the high CO2 could be attributed to reactions between CO and oxygen from adsorbed air in the bagasse. According to Di Blasi et al (1999), the relatively high amount of carbon dioxide is due to the presence of a high amount of oxygen in bagasse which constitutes about 43 wt % of bagasse on dry basis. (Refer to ultimate analysis of bagasse on Figure 2-1).

Table 7-4 Gaseous components distribution from pyrolysis (% volume)

	Garcia-Perez et al (2002)	Batch Pilot Plant
Carbon dioxide	48.2 – 56	70.4
Carbon monoxide	28.6 – 31.8	23.4
Ethane and ethane	0.9 – 1.5	0.3
Propane and propene	1.3 – 2.1	< 1.0
Hydrogen	1.1 – 2.4	0.1
Methane	2.2 – 6.7	4.7

Details of variation in gas production with temperature during pyrolysis of bagasse are shown in Figure 7-14 and Figure 7-15. The results show that CO2 and CO gases are liberated around 100 - 280°C following the thermal decomposition of polyscaccharides, hemicellulose and cellulose. From 300 to 400°C, there was a drop in CO and CO2 yields because hemicellulose and cellulose thermal decomposed and contributed mostly to volatiles (and subsequently liquid tars). The exothermic decomposition of lignin and other extractibles at 310 to 450°C produced pyrogas rich in CO, CH4 and liquid tars after which the pyrogas production decreased. These results agree with Rodriguez (1993) and the slight shift of events could be due to the gas generation-to-sampling delays in the gas analysis system. According to Di Blasi et al (1999), a gas-liquid separation train coupled with a low off-gas flowrate can introduce significant delays in gas collection and analysis such that the temperature in the reactor and species evolution profile become two separate processes. Additionally delays could be attributed to existence and accumulation of gas pockets in the reactor. These gas pockets gave rise to a 'damped wave' pattern in the species' evolution profiles.

According to Encinar *et al* (1997), temperature has a positive effect on methane and hydrogen production and a negative effect on carbon dioxide. CO_2 was expected to rise at high temperatures but because of gasification reactions with carbon, it was reduced to zero giving rise to an increase in carbon monoxide at temperatures above 700°C. The evolution of hydrogen was very low at low temperatures because its production is negligible at these temperatures but rapidly rose above 700°C possibly due to the water-gas shift reactions. The production of hydrogen during pyrolysis is therefore negligible.

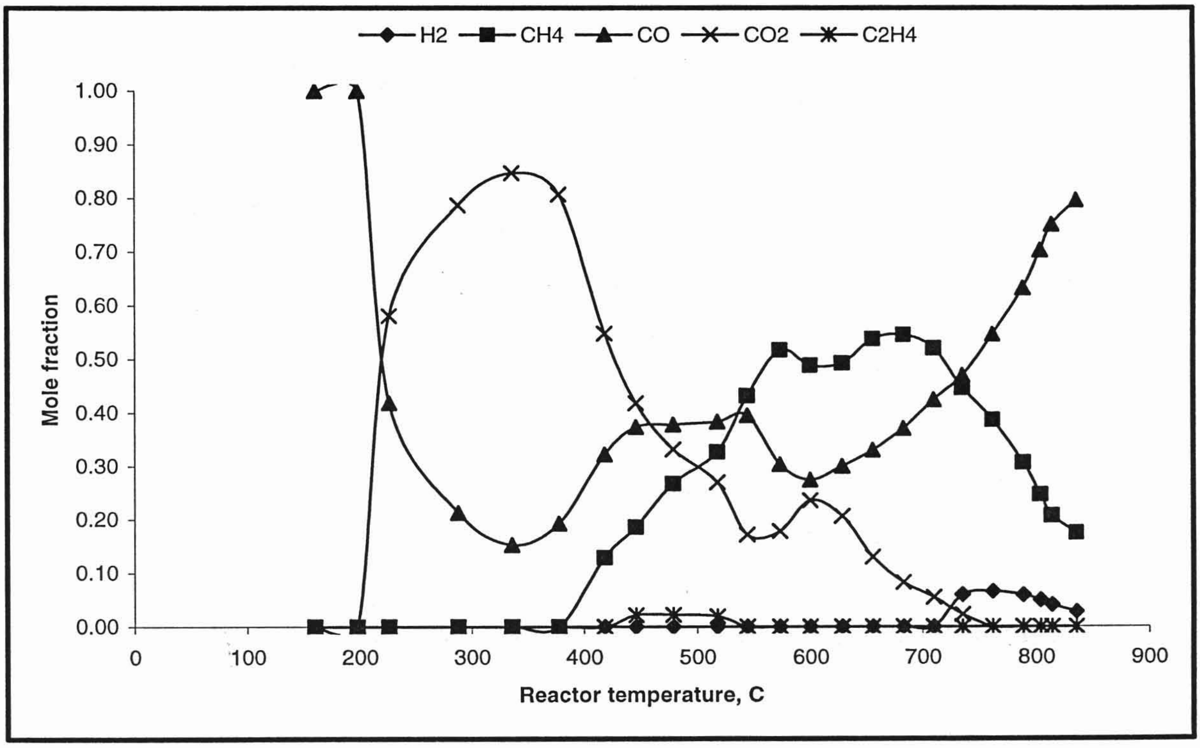

Figure 7-14 Effect of temperature on molar fraction of the gases

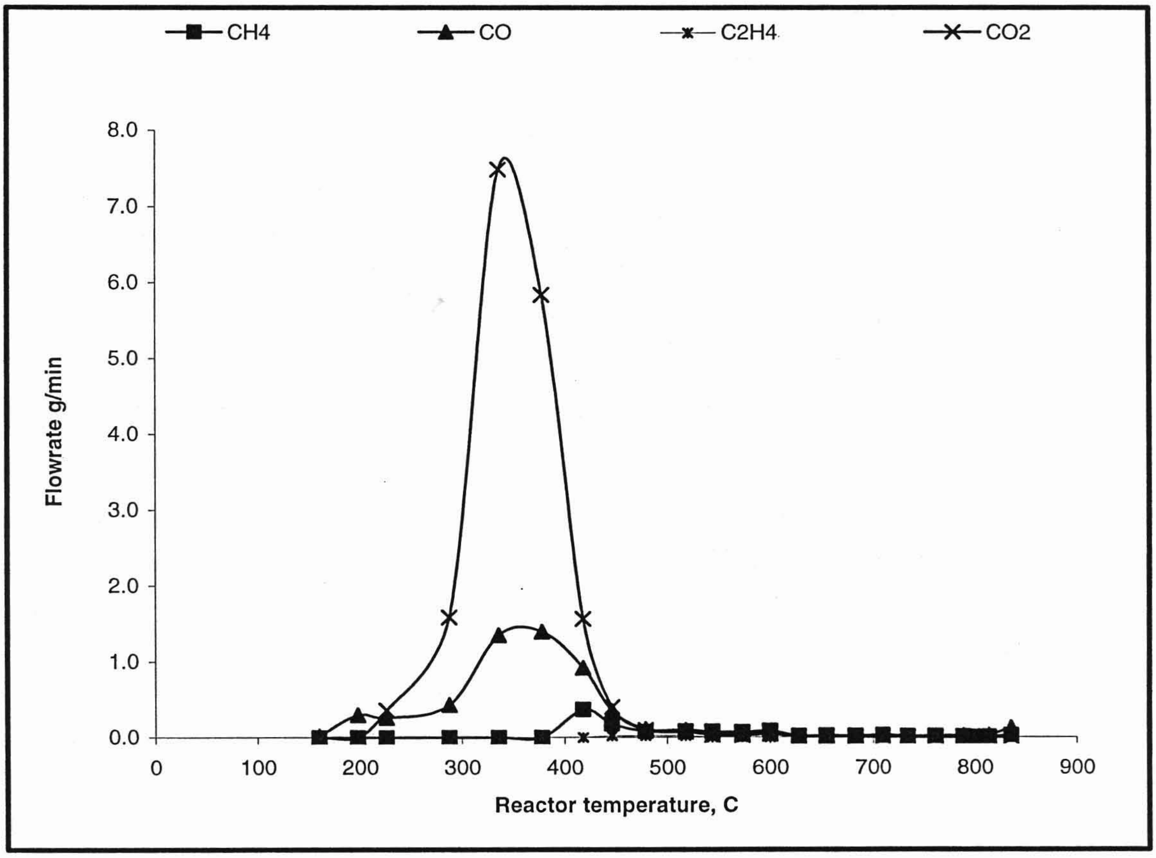

Figure 7-15 Rate of evolution profiles of pyrolysis gases produced at 700°C

7.7. Summary of potential heat in process by-products

In order to check self-sufficiency in the case of continuous bagasse pyrolysis and char activation, the amount of potential energy available in the by-products was calculated. From the thermal calculations, Table 7-5 and Table 7-6, pyrolysis by-products have a total potential heat of combustion of 63 MJ/kg of active carbon produced. The activation gaseous products also have a collective 31 MJ/kg of active carbon produced. Also available was the sensible heat at 10 and 36 MJ/kg of active carbon from pyrolysis and activation respectively. On analyzing the gas components, the existence of CO_2 in both pyrolysis and activation by-products was above the expected values implying that some of the CO was oxidized by oxygen. Also the absence of hydrogen in the activation gases could have been a result of oxidation reactions. This represents an energy loss of at least 21MJ/kg of active carbon, about 19% of the potential heating value of the total combustibles. An assumption was made that 94MJ would be available to the process at furnace efficiency of about 80%.

The gas analysis experiments were carried with the aid of a vacuum pump to draw off-gases from the reactor flue line to the GC. The negative pressure could have allowed air into the system hence the high CO_2 and absence of H_2. The main reason why vacuum was used during gas analysis was because of the low gas flow rates from the kiln which were not enough to provide positive pressure for gas sampling and injection into GC.

Table 7-5 Combustible by-products of pyrolysis (Basis of 1kg of active carbon)

	Temperature °C	**Calorific Value MJ/kg**	**Sensible heat MJ/kg**
Hydrogen	700	0.012	0.001
Carbon monoxide	700	5.554	0.410
Methane	700	3.142	0.143
Carbon dioxide	700	0.000	1.933
Ethylene	700	0.291	0.013
tar	700	53.651	2.521
Aqueous phase	700	-	5.232
Total		62.65	10.254

Table 7-6 Combustible by-products of activation (Basis of 1kg of active carbon)

	Temperature °C	**Calorific Value MJ/kg**	**Sensible heat MJ/kg**
Carbon monoxide	850	7.764	0.709
Carbon dioxide	850	0.000	3.142
Methane	850	23.449	1.381
Steam	850	-	31.045
Total		31.213	36.277

7.8. Decolourisation of sugar solutions using BPAC

The adsorption of activated carbons is not only determined by its total surface area, but also by its internal porous structure and surface chemistry. A detailed discussion on the important properties for sugar colour removal is in Chapter 3. According to Bansal (1988), carbon surfaces have a pore size that determines its adsorption capacity, a surface chemistry that influence its interaction with polar and non-polar adsorbates and active sites that determines the type of reactions with other molecules. Experiments were carried out by Singh (2004) at SMRI to determine the performance of BPAC compared to commercial products such as Norit PN2, PCX and P9-45. All experiments were conducted using PACs.

Experiments were carried out with varying amounts of carbon at the rate of 0.5, 1.0, 1.5 and 2.0 g/100 °Brix of brown liquor. The experimental method and raw data is shown in Appendix D section D.4. The final results are shown in Figure 7-16. The BPAC was lower by 20% of colour removal compared to the best active carbon (PCX) at a carbon dosage of 0.5% but its performance improved significantly with increase in dosage rate until it was within 5% at a carbon dosage rate of 2%. About 70% colour removal was achieved at a dosage rate of 0.5g carbon / 100 °Brix which was comparable to Norit PN2 carbon. At higher carbon to Brix ratios, there was faster adsorption of colour onto the adsorbent surface that produced a lower final Brix. This was attributed to the fact that a fixed amount of carbon adsorbs a certain amount of colourants, therefore the more the dosage the larger the amount of carbon of colour that can be removed.

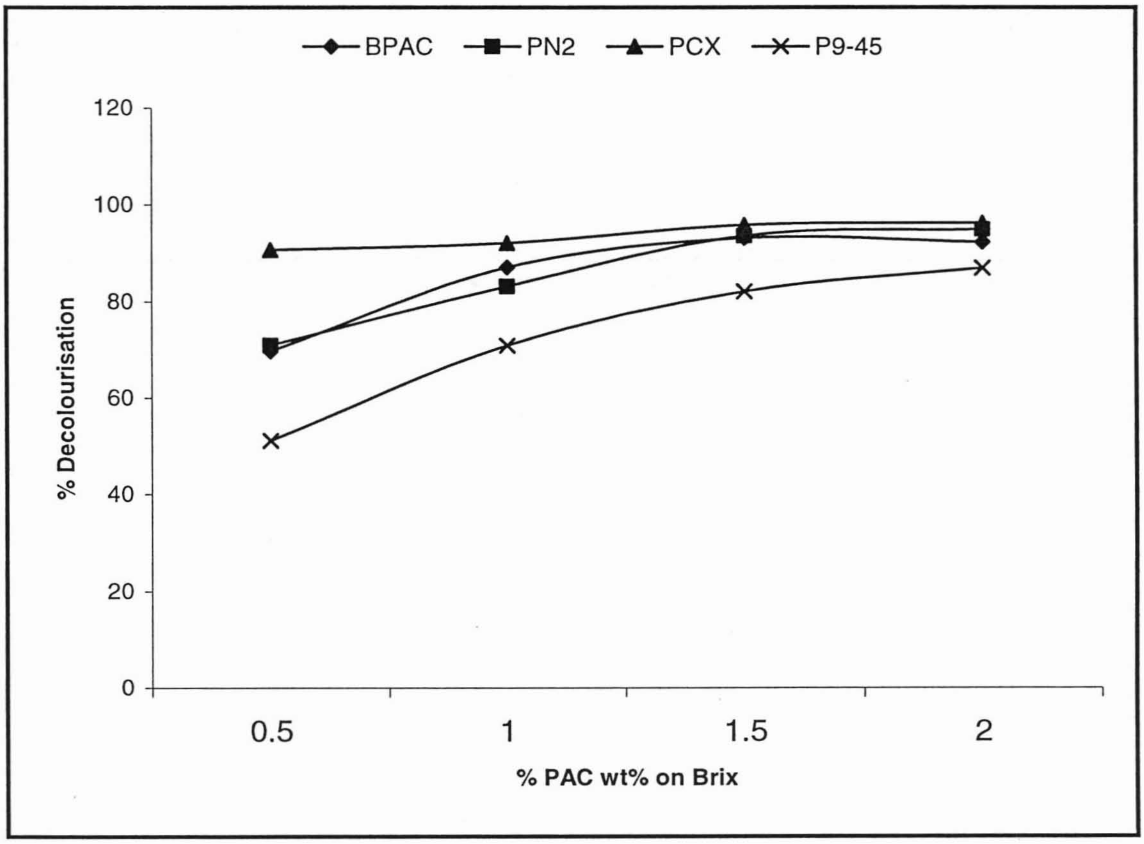

Figure 7-16 Decolourisation of brown liquor (65°Brix) by powdered active carbons (Singh, 2004)

BPAC and Norit PN2 were further investigated to find the effect of the concentration (°Brix) of the sugar solution on the performance of the carbons. The reason for further comparing BPAC with Norit PN2 was that Norit PN2 is the most common used PAC in sugar industry. This was important for the purposes of finding a cheaper alternative adsorbent to Norit PN2. The experimental procedure and raw data is shown in Appendix D section D.5. Clear juice at 12°Brix was heated and concentrated to different levels before adding carbon at about 0.5% on Brix. The results are shown in Figure 7-17. The results illustrate the superior quality of BPAC to Norit PN2. Norit PN2 is one of the PACs that are currently used in sugar industry for colour removal in the refineries. BPAC had twice as much adsorptive capacity compared to Norit PN2. The adsorptive capacity of BPAC increased with brix up to a maximum of 22.7% at 39°Brix while the optimum concentration for Norit PN2 was 33.5° Brix with a colour removal of 12.3%. The initial increase could be attributed to the fact that carbons can adsorb a certain amount of adsorbate and hence colour removal increased as long as the ratio of the available active sites could accommodate the available colourants. As the concentration of colourants were increased, there was a stage when the active sites in the carbons failed to copy with increasing number of colourants leading to a reduction in colour removal percentage.

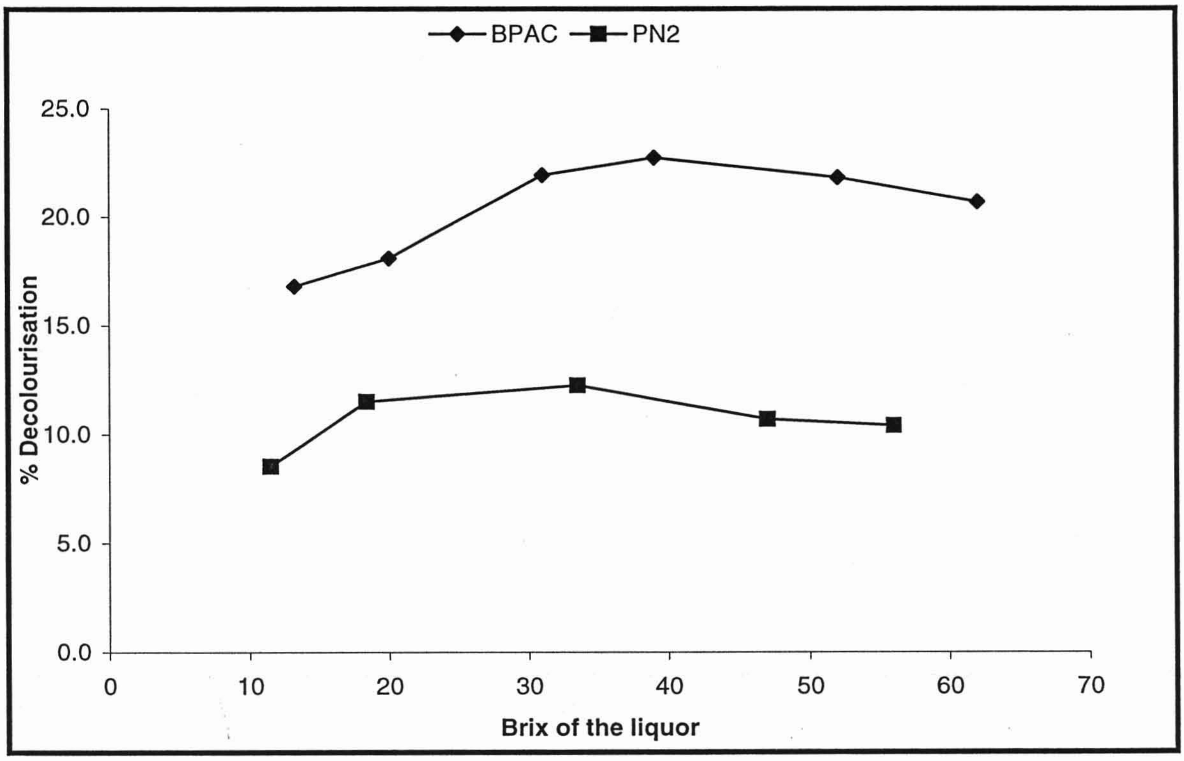

Figure 7-17 Effect of Brix on decolourisation (Singh, 2004)

The kinetics of a process is important due to its direct influence on production rate. An investigation was carried out using Norit PN2 and BPAC to establish the effect of contact time on colour removal. According to Vadivelan and Kumar (2005), the prediction of batch adsorption kinetics is necessary for the design of industrial adsorption coloumns. The nature of the adsorption process will depend on the physical and chemical properties of the adsorbent system and the conditions. The experimental procedure and raw data is shown in Appendix D section D.6. The final results are shown in Figure 7-18. There was an increase in colour removal with increase in contact time. BPAC showed its superior quality again with twice as much adsorption as Norit PN2 for residence times of 40, 60 and 120. From the results the colour removal was faster within the first 40 minutes and thereafter proceeded at a slower rate until eventually getting saturating. The high initial adsorption rate could be attributed to a high amount of active sites available for adsorption and the high concentration gradient between the colourants in the solution and those on the carbon surface. As time went by the active sites got saturated and consequently the concentration gradient of the colourants was reduced.

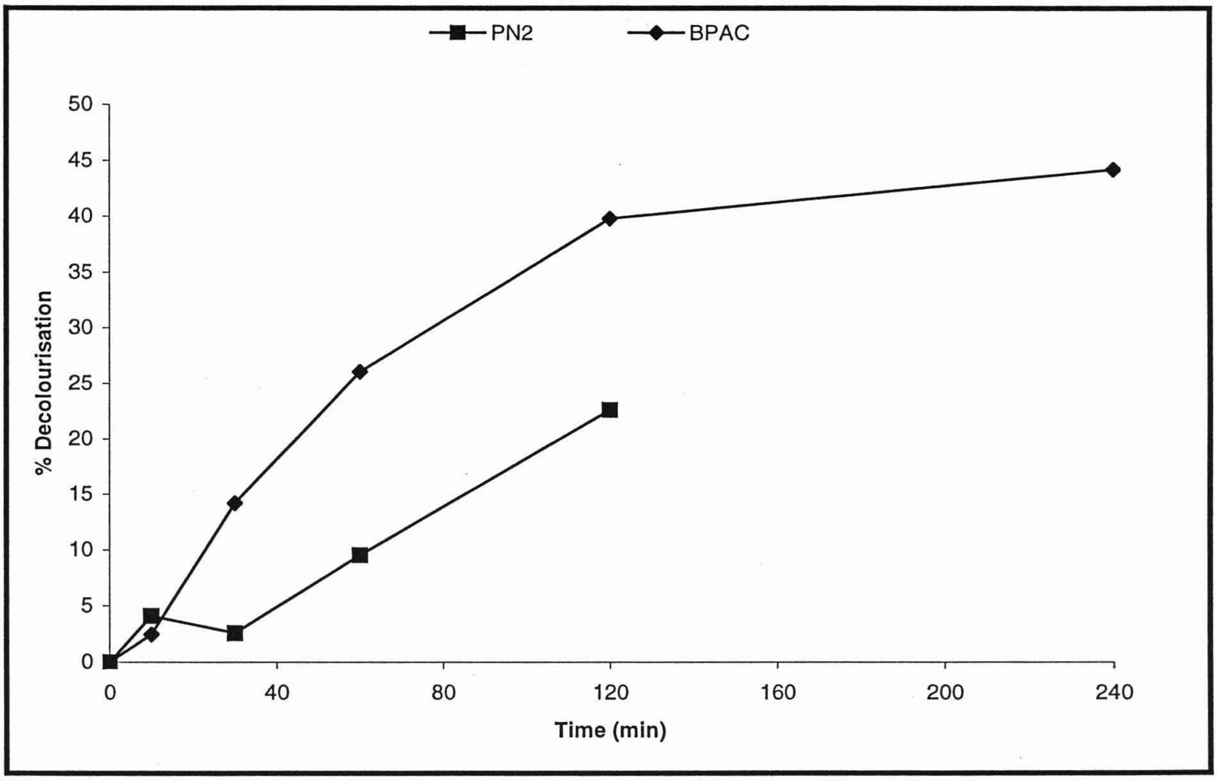

Figure 7-18 The effect of residence time on colour removal (Singh, 2004)

Experiments were carried out to find the optimum quantity of carbon for colour removal in a simulated sugar evaporation process. The experimental procedure and raw data is shown in Appendix D section D.7. The final results are shown in Figure 7-19. It is clear that BPAC out performed Norit PN2. However there was a significant decrease in the amount of colour removed with increasing adsorbent mass and this could be attributed to the concentration gradient between the colourants in the solution and those adsorbed. An optimum carbon dosage rate of 1% was chosen and the corresponding colour removal percentages were 36% and 20% for BPAC and Norit PN2 respectively.

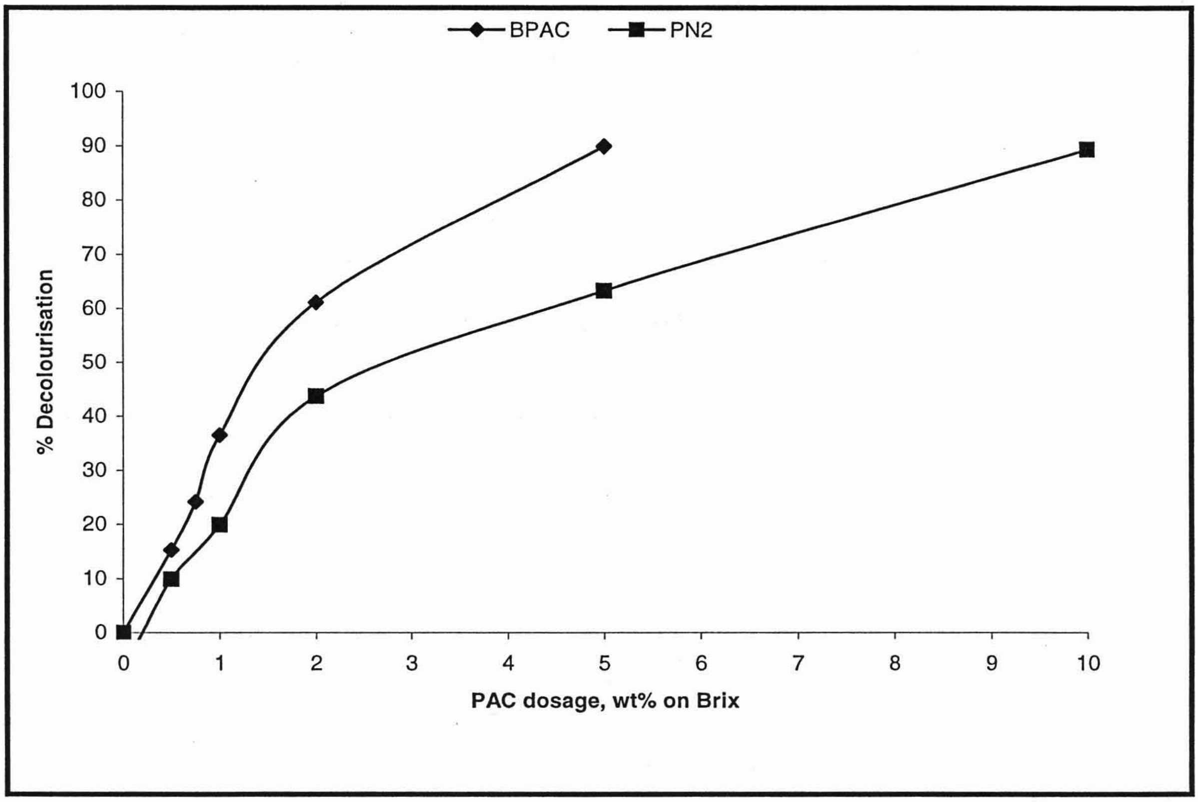

Figure 7-19 Decolourisation during evaporation of clear juice from 12-65°Bx (Singh, 2004)

7.8.1. Adsorption isotherms

The adsorption isotherms provide fundamental physiochemical information for evaluating the applicability of the adsorption process as a unit process for colour removal. The sugar decolourisation isotherms were investigated using the two commonly used isotherms; Freundlich and Langmuir isotherms. The full equations are discussed in Sections 6.4.2.1 and 6.4.2.2 and the raw data is shown in Appendix D section D.8. The final results of the Freundlich and the Langmuir analysis are plotted in Figure 7-20 and Figure 7-21 respectively.

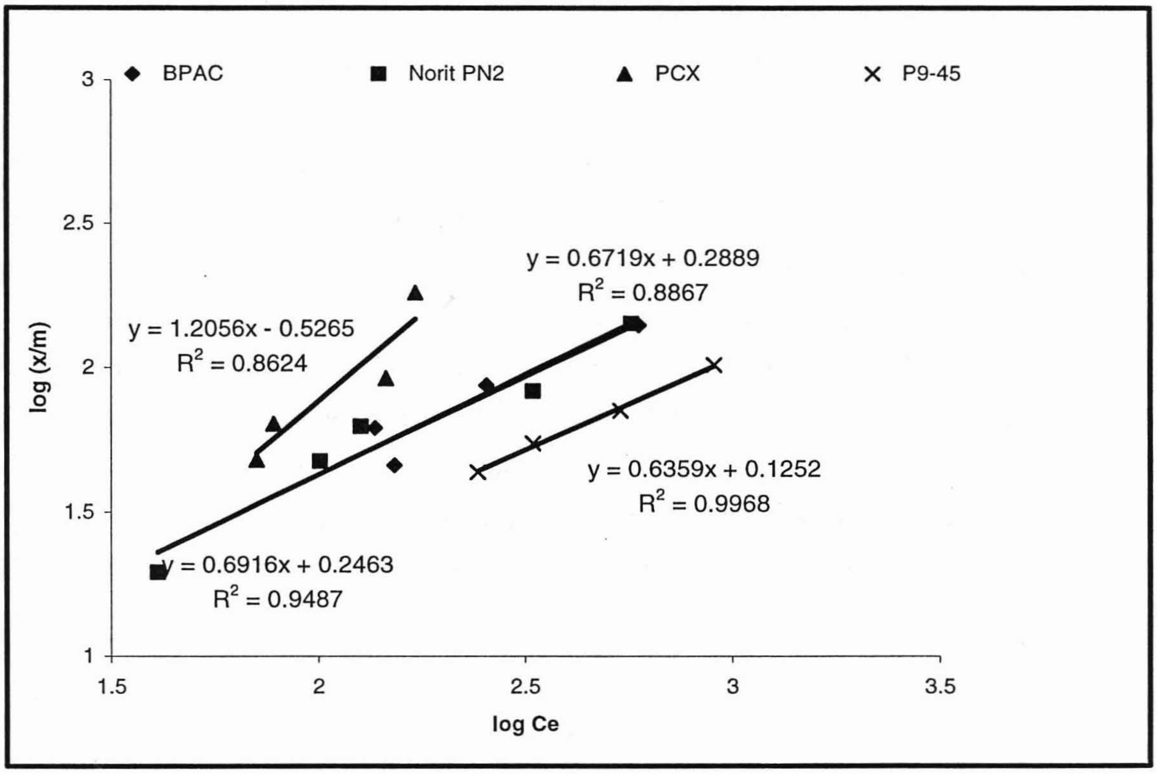

Figure 7-20 Freundlich Isotherms for sugar decolourisation using PACs

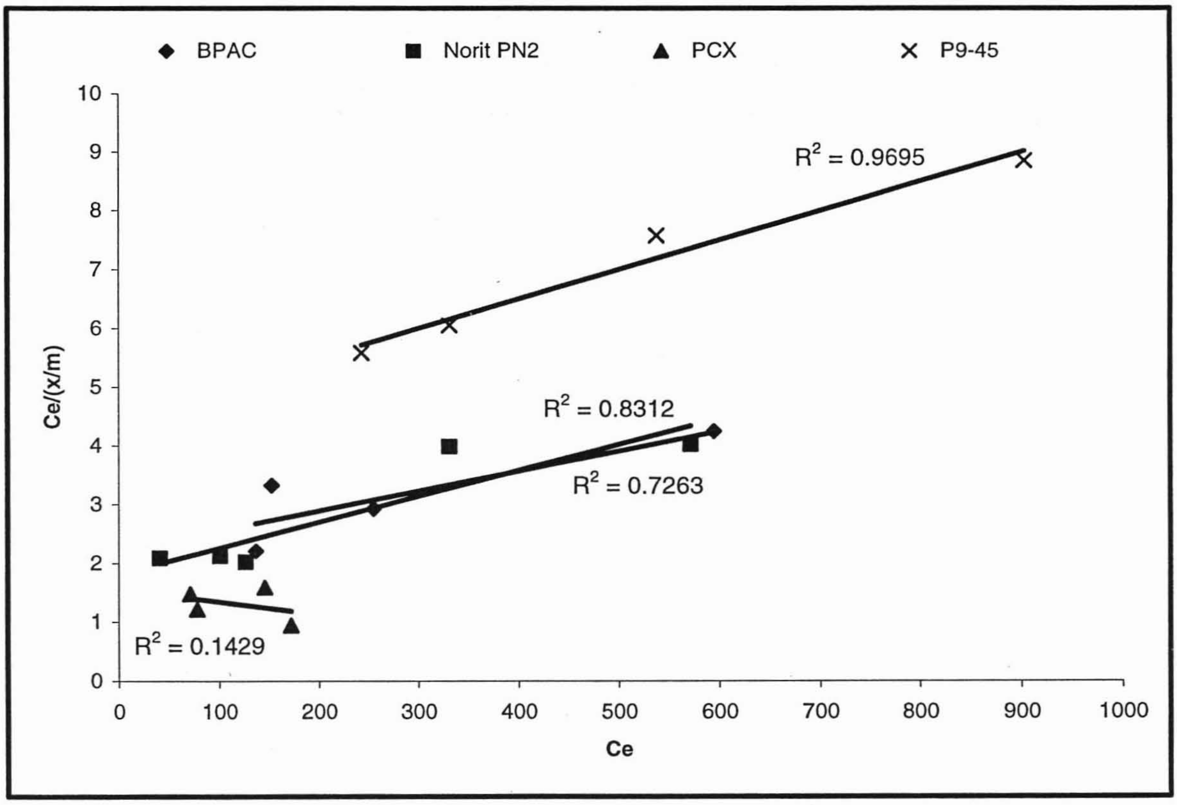

Figure 7-21 Langmuir isotherms for sugar decolourisation using PACs

The results show that the Freundlich isotherms described the sugar adsorption data better than the Langmuir isotherms for most of the PACs after considering the R^2 values.

The constants K and n were determined from the Freundlich plot and the results are summarized in Table 7-7. The constant K, partition coefficient in equilibrium, represents the quantity of colour adsorbed into the carbon adsorbent for a unit equilibrium concentration, while n is a rough estimate of the intensity of adsorption. The slope (1/n) measures surface heterogeneity. Heterogeneity becomes more prevalent as 1/n gets closer to zero. BPAC had the highest adsorption capacity (K value) compared to the other PACs with a relative adsorption capacity of 1.945g of colour per g of carbon. The value of $0.1 < 1/n_c < 1$ indicates favourable adsorption (Vadivelan *et al* 2005; Krishman and Anirudhan, 2002). The value of n for BPAC was 0.672. The higher the values of $1/n_c$ the better the adsorptive forces operating on the surface of the adsorbent, and PCX had the best adsorptive forces.

Table 7-7 Summary of the Freundlich constants for different PACs

	K, g/g	**$1/n_c$**	**R^2**
PCX	0.2975	1.206	0.86
Norit PN2	1.763	0.692	0.95
BPAC	1.945	0.672	0.89
P9-45	1.334	0.636	0.99

PROCESS DESIGN

The commercial plant design was based on results derived from investigations on drying, pyrolysis and activation of bagasse and the decolourising effect of BPAC on clear juice. Experiments on thermal degradation of bagasse showed that the best BPAC is produced by carbonization at 700°C for a hold time of 1 hour followed by steam activation at 850°C for an activation time of 1hour. The best active carbon had an MBN of about 257mg/g, a quality similar to the one produced by Devnarain (2003). Sugar adsorption results showed that 500kg/h of activated carbon would be required to treat 600 m^3/h of clear juice at 12°Brix to give 20% colour removal at dosage rate of 0.70wt% BPAC. The two-stage physical process gave an activated carbon yield of 7wt% on dry bagasse basis. A carbon production rate of 500 kg/h would require a wet bagasse feed (50% moisture content) of about 21.4t/h. At a bagasse screening rate of 61.7% on mass basis, the effective process requirement would be about 13.3t/h. That gives about 315 t/day using three – eight hour working shifts and 22 working hours per day). Taking a 240 day working cycle per year that corresponds to a sugar mill crushing season, the total wet bagasse requirements is about 71 000 tonnes against a probable surplus of about 132 000 tonnes of bagasse at a mill crushing rate of 500 tch provided there is no cogeneration.

8.1 Conceptual process design and integration

Initial conceptual design was carried out by Devnarain (2003) who investigated the technical feasibility of producing BPAC from diffuser bagasse using a thermo-balance and also characterized the product quality. Following investigations on scale-up effects on the production of BPAC in a rotary batch kiln another conceptual design of the demonstration plant was made to provide detailed information on economic and environmental impact. A robust simulation of the conceptual design on Excel spreadsheet provided necessary information on probable heat recovery and cycles. The final process flow diagram is in Figure 8-1. According to Harmsen (2004), conceptual design methods are applied in industry to obtain processes at lower cost and energy requirements. In view of the Kyoto Protocol, businesses have to be innovative enough to come with new designs with savings on energy, capital expenditure and cost of raw materials compared to old processes.

8.1.1 Process description

The main goal of the project was to produce activated carbon from diffuser bagasse at the same time taking advantage of the combustible gases to minimize energy costs. From the experimental results, the following steps were adopted for the commercial plant design:

1. transfer and screening of fresh bagasse
2. drying (maybe use the steam for steam activation)
3. storage of dry bagasse
4. pyrolysis
5. activation using exhaust steam from the mill
6. separation of combustibles from condensables
7. recycling and reuse of pyrolysis and activation gases for process energy requirements
8. recycling furnace flue gases for drying bagasse

Fresh bagasse is carried by conveyor from the drying mills to the boilers in the sugar mill. With the aid of an adjustable plough, part of the bagasse goes to the BPAC plant. A conveyor leads the raw bagasse into a rotary drum sieve where the fine material and sand is sifted out to give about 60 – 70 wt% (wet basis) of screened feed. The fines are conveyed back to the boilers where they are burned for steam production. The screened fraction is transferred to an indirect contact dryer by a conveyor. Hot gases at 700°C from the direct cooler are used for drying the wet bagasse by heat conduction via a wall to moisture levels below 2% at a dryer operating temperature of about 200°C. After drying, the temperature of the hot gases is reduced to about 225°C. An induced draught fan (ID fan) is used to suck the drying gases from the dryer (jacket side) and blows them out via the stacks. The dry bagasse is screw fed and pyrolysed in an indirect fired kiln. During pyrolysis bagasse is heated up to 700°C at a heating rate of 10 °C/min and kept at this temperature for 1 hour to give a char yield of about 22wt%. Then the bagasse char formed is transferred to another indirect fired rotary kiln for steam-activation at 850°C to give an activated carbon yield of 7wt%. The activated carbon is collected in a quencher and sent directly to the sugar mill for sugar decolourisation. However some of the heat energy in the hot activation gases (at 850°C) is recovered by passing the gases though a counter-current heat-exchanger where the temperature of the activating (exhaust) steam from the mill is raised from about 150°C to 750°C. The pyrolysis vapours and activation gases are then collected and taken to a condenser where the condensable liquids are separated from the incondensables gases. The liquids are separated using decanting to give tar and an aqueous phase (mainly water and some hydrocarbons). The liquid tar and gases (from activation and pyrolysis) at ambient temperature are fed into the pyrolysis and activation furnaces where combustion takes place at about 1400°C using 70% excess air. Temperature is critical because the heat provides the driving force to sustain combustion. So auxiliary burners may be supplied to preheat the chamber or support combustion. Hot gases from the pyrolysis and activation furnaces at 1400°C are directly mixed with ambient air in the direct cooler to a temperature of 700°C for drying bagasse. The energy flow diagram is shown in Figure 8-1 and mass and energy steams are summarized in Table 8-1.

Table 8-1 Mass and energy streams (Basis of 500kg/h of BPAC)

Flow	**Material**	**Mass, t/h**	**Temperature °C**	**Energy, GJ/h > 25°C**
1	wet bagasse	21.4	25	0.0
2	screened bagasse	13.3	25	0.0
3	fine bagasse	8.1	25	0.0
4	water vapour	6.8	200	17.9
5	dry bagasse	6.5	200	1.5
6	char	1.4	700	1.6
7	pyrogas and vapours	5.1	700	5.1
8	BPAC	0.5	850	0.7
9	superheated steam	5.0	750	7.6
10	exhaust steam	5.0	150	1.0
11	activation gas	5.9	850	8.9
12	activation gas	5.9	260	1.5
13	combustibles	4.6	25	0
14	Condensates/water	6.4	25	0.0
15	flue gases	15.5	1400	28.5
16	air	19.7	25	0.0
17	diluted flue gas	35.2	700	28.5
18	diluted flue gas	35.2	225	8.5
19	**air (70% excess)	10.9	25	0.0

**Calculated using the information in Appendix H

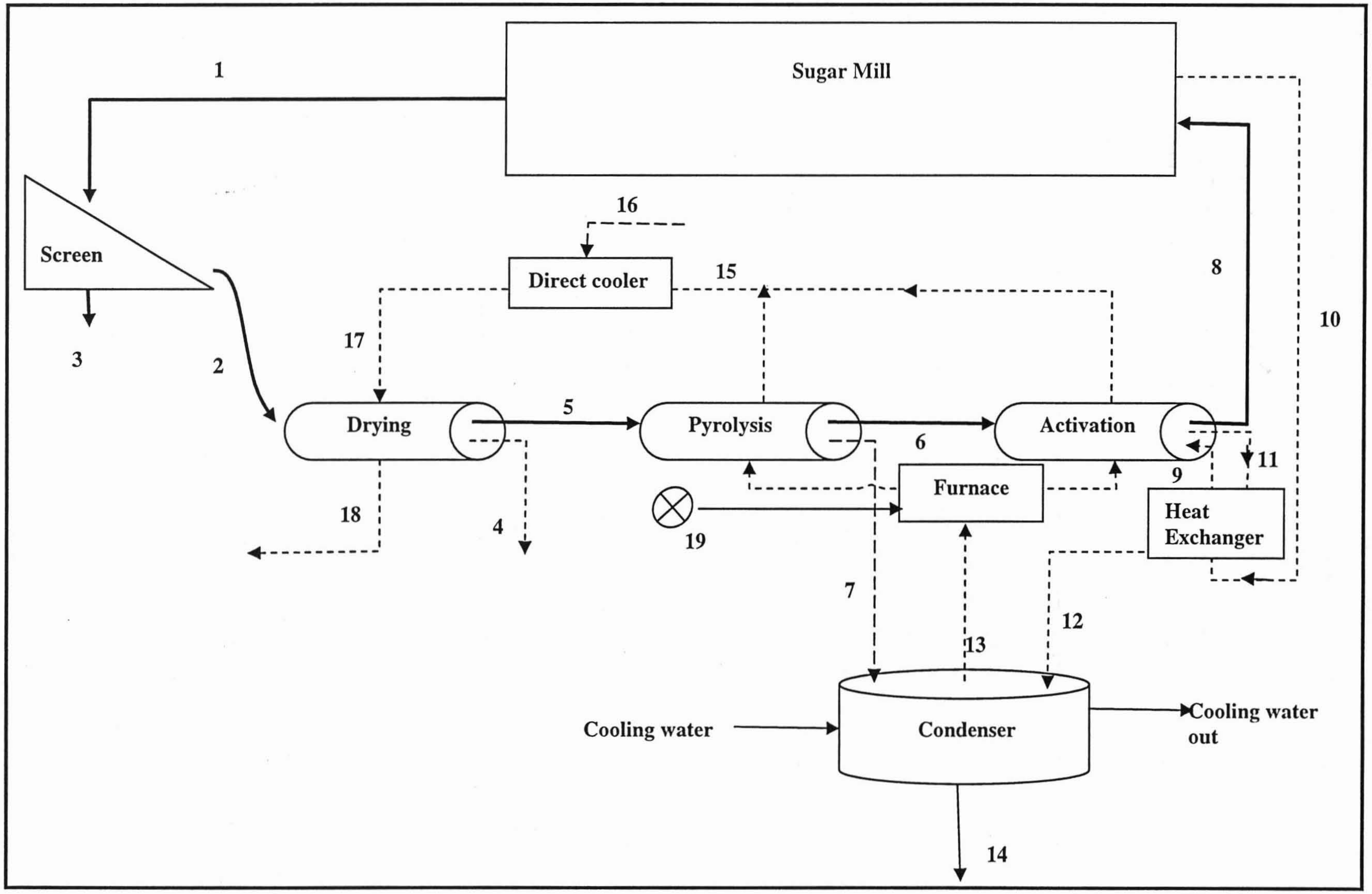

Figure 8-1Conceptual design flow diagram for manufacture of BPAC

8.2 Process Integration of the BPAC plant within a sugar mill

The activated carbon plant will be situated within a sugar mill. Ko *et al* 2004 considered two process scenarios for a waste tire pyrolysis plant, a stand alone and one as an integral part of a cement factory. The latter scenario proved to have significant financial benefits. It is expected that siting the activated carbon plant at a sugar mill will significantly lower the total capital and operating costs of the new project and make the ROI more attractive. This stems from the fact that the two plants will be able to share existing structures at the same time there are other potential energy recovery options available to both. The close proximity eliminates the need for transporting raw materials and products over long distances among other advantages as shown in Figure 8-2.

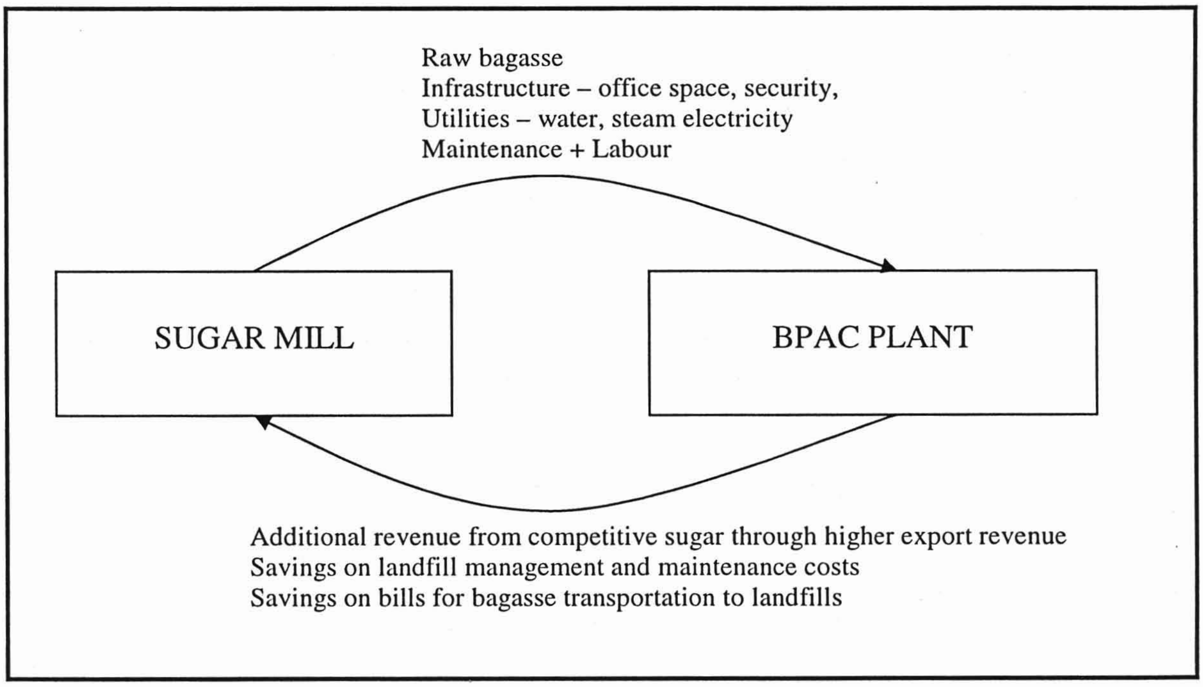

Figure 8-2 Symbiotic relationship between the sugar mill and the BPAC plant

8.3 Economic Analysis

8.3.1 Process Simulation

A material and energy balance simulation program of the activated carbon process was developed to carry out the costing and economic evaluation of the system. The mass and energy balance calculations were based on the principle of conservation of mass and energy in a continuous steady-state process as shown in Appendix C. The general mass balance equation is:

$$input + generation = output + consumption + accumulation$$

The mass and energy balance is based on the proposed conceptual design for an activated carbon manufacturing plant at one sugar mill in South Africa. The process material and energy balances were conducted on an EXCEL spreadsheet based on experimental results as shown in Table 8-2.

Table 8-2 Summary of the energy Balance (Basis of 1kg of activated carbon)

	Mass Kg	Initial Temp. °C	Final Temp. °C	$\Delta H_{sensible}$ MJ	$\Delta H_{reaction}$ MJ	ΔH_{total} MJ
Drying						
heat up wet bagasse	26.51	25	200	38.62		38.6
flue gases		25	225			17.9
Pyrolysis						
heat up char + gases	12.99	25	700	13.47		13.5
Activation						
heat up carbon + gases	12.86	25	850	19.10		19.1
Reactions						
activation			25		20.99	21.0
Total Outputs						**110.1**
Pyrolysis						
dry bagasse	12.99	25	200	2.95		3.0
Activation						
char	2.86	25	700	3.28		3.3
steam		25	150	1.98		2.0
Reactions						
combustion			25		93.32	93.3
pyrolysis			25		8.57	8.6
Total Inputs						**110.1**
Difference (Nett Energy per kg of BPAC)						**0.0**

Energy calculations shown above show that the heat released by burning combustibles and enthalpy available in hot gases is enough to satisfy the plant thermal energy needs. This agrees with work done by Zandersons *et al* (1999), Ng *et al* (2002) and Antal Jr. *et al* (2000). However reduced thermal efficiencies in rotary kilns of about 45 – 80% (Perry, 1997) could require installation of supplementary fuel lines to offset losses and energy fluctuations in the process. Another difficulty in the calculation is the enthalpy of pyrolysis which differs from one author to another as illustrated in Appendix I. In the above calculations, $\Delta H_{pyrolysis}$ was assumed to be exothermic, -0.66MJ/kg (Antal, 2003).

8.3.2 Economic evaluation

The aim of the economic evaluation is to present information regarding the economic feasibility of establishing a demonstration plant at one of the sugar mills. The technical feasibility of the project in terms of production of activated carbon and its corresponding decolourising effect on sugar juices, and process design and integration have already been discussed. The economic evaluation exercise is based on an activated carbon plant with a capacity of 500kg/h.The plant will operate 22 hrs a day using a three-eight hour working shift and 240 working cycle per year. The total wet bagasse requirement is about 75,000 tons.

8.3.3 Plant equipment costs

The equipment costs information was obtained from Matches Company and reference books (Perry, 1997; Peters and Timmerhaus, 1980). Plant equipment costs can be updated using the Marshall and Swift Index as shown below:

$$\text{cost of plant item (2005)} = \text{cost of item (20XY)} \times \left[\frac{\text{cost index 2005}}{\text{cost index 20XY}}\right]$$

Equipment sizing and costing for major equipment is shown in Appendix E. The expected error into the factored costing estimation is +/- 20 – 30% (Choy *et al* 2004). The total costs of the major equipment items for manufacture of activated carbon from bagasse was estimated to be US$4 million inclusive of 15% delivery costs as shown in Table 8-3.

Table 8-3 Delivered Equipment costs

Equipment	**Cost**
Dryer	$1,144,500.00
Pyrolysis and activation kiln	$2,300,000.00
Bins - an hours feed	$20,300.00
Rotary trommel	$50,000.00
Delivery costs	$527,220.00
Total	**$4,042,020.00**

8.3.4 Total capital investment

The sum of the fixed capital investment and the working capital is known as the total capital investment. The fixed capital investment represents money required to install process equipment with all auxiliaries that are needed for complete process operation and includes the direct and indirect costs while the working capital is necessary for plant operation. The capital investment was estimated using well accepted ratios based on the capital cost of equipment. This method is also applied by International Furan Chemicals (IFT) for preliminary design stages (Wilson and Buzzard, 2005). The cost of the activated plant is calculated by multiplying the total equipment cost by some factor to get an estimate of the total capital investment and the results are shown in Table 8-4.

Table 8-4 Summary of the total capital investment of the BPAC plant

	Percentage	**Amount**
Delivered equipment cost		$4,042,020.00
Total direct plant costs	70% of delivered equipment costs	$2,829,414.00
Indirect costs	25% of delivered equipment costs	$1,010,505.00
Working capital	3 months of sales	$1,296,000.00
Subtotal		**$9,177,939.00**
EIA and Hazop	4% of fixed capital investment	$315,277.56
Contingency	10%	$949,321.66
Total capital investment		**$10,442,538.22**

8.3.5 Direct costs

The direct-costs items that are incurred in the construction of a plant include:

1. purchased equipment erection
2. piping, including insulation and painting
3. electrical equipment and materials, power and lighting
4. instrumentation and controls
5. process building and structures
6. site development
7. service utilities for steam, water, power, air and fire fighting services
8. land

The total direct costs for constructing the BPAC plant were estimated at US$2.8 million.

8.3.6 Indirect costs

The indirect cost items incurred include:

1. engineering and supervision
2. continuous emission monitoring
3. construction expense - contractors fee and

The total indirect cost for the BPAC plant was estimated at US$1.01 million.

8.3.7 Working capital

Most chemical plants use an initial working capital of 10 – 20% of the total capital investment and this can go as high as 50% depending on the level of inventory. The working capital includes:

1. money invested in raw materials and supplies in stock
2. finished products in stock and semi finished products in process of being manufactured
3. accounts receivable
4. cash kept on hand for monthly payment of operating expenses – salaries, wages and raw material purchases
5. accounts payable and
6. taxes payable

An initial working capital of 15% of the delivered equipment costs was assumed for the BPAC plant. This translates to working capital of US$1.3 million. The total cost of the EIA and HAZOP was estimated at US$0.3 million. Adding the direct costs, indirect costs, working capital and cost for EIA and HAZOP gives a total capital investment of US$10.44 million for the BPAC plant.

8.3.8 Fixed operating costs

Fixed operating costs are expenses that are practically constant from year to year and do not vary widely with changes in production rate. These are bills that have to be paid whatever the quantity of 'product' is produced. A summary of the factors making up the fixed operating costs is given in Table 8-5. The fixed annual operating costs for a BPAC plant were estimated at US$0.9 million.

Table 8-5 Summary of the fixed operating costs and its factors

Maintenance	6% of fixed capital investiment	$472,916.34
Operating labour	3 workers x 3 shift per day (U$5/h)	$86,400.00
Supervision and clerical	20% of operating labour	$17,280.00
Laboratory	15% of operating labour	$12,960.00
Plant spares	15% of maintenance	$70,937.45
Insurance	1% of fixed capital investiment	$78,819.39
Royalties and patents	4% of revenue	$209,088.00
Fixed annual operating costs		**$948,401.18**

8.3.9 Variable operating costs

Variable operating costs include expenses directly associated with the manufacturing operation and they are dependent on the amount of product produced. A summary of the factors making up variable operating costs are given in Table 8-6. The cost of bagasse was quoted at the coal replacement value of 3.6t of bagasse (Paturau, 1969) to give an average value of about US$12.33. The total annual variable operating costs was US$1.27 million. Adding the total variable operating costs to the total fixed annual operating costs yields an estimated total annual manufacturing cost of US$2.22 million.

Table 8-6 Summary of the total variable operating costs

raw materials - wet bagasse	75000 tonnes	$924,750.00
utilities	8% of delivered equipment costs	$323,361.60
miscellaneous materials	5% of maintenance	$23,645.82
variable operating costs		**$1,271,757.42**

8.3.10 General expenses

General expenses are costs that are involved in any company operation and a summary of the factors involved is given in Table 8-7. The total annual general expenses were estimated at US$0.51 million.

Table 8-7 Summary of the total general expenses

Administrative expenses	15% of the total labour and maintenance	$86,489.45
Sales expenses	11% of the total manufacturing costs	$244,217.45
Research and development expenses	8% of the total manufacturing costs	$177,612.69
Total general expenses		**$508,319.58**

8.3.11 Total production costs

The total production cost is calculated on annual basis and generally consists of manufacturing costs and general expenses. In turn the manufacturing cost consists of fixed operating costs and variable operating costs. The general expenses are involved in any company's operation. The total annual production costs were estimated at US$2.7 million as shown in Table 8-8.

Table 8-8 Summary of the total annual production costs

Fixed annual operating costs	$948,401.18
variable operating costs	$1,271,757.42
total general expenses	$508,319.58
total production costs	**2,728,478.18**

8.3.12 Revenue from BPAC Project

An estimated US$2.7 million would be required to produce about 2880 tons of BPAC and this gives a product cost price of about US$0.95 per kg. From literature the selling price of activated carbon varies with its activity. The price of activated carbon largely depends on its quality and the selling price range from US$0.82 in China to US$3.11 in Japan per kg (Choy *et al* 2005). According to Ng *et al* 2002 active carbon for niche markets can sell for US$4 while low quality for water treatment sells for only US$1 per kg. Hence based on the fact that the product might be faced with intense competition from China, the selling price of BPAC was initial set at US$1.80/kg, which gives about US$5,184,000.00 in sales revenue. Additional revenue would be sourced from savings against costs associated with maintaining a bagasse heap (transport, labour and risk of fire etc) which was assumed at US$43,000 and use of saturated BPAC for boiler feed at about US$36,000 to give annual total revenue of US$5,227,200.00.

8.3.13 Return on Investment

A simple estimate of the return on investment for the BPAC project was calculated before the detailed evaluation. A positive ROI means that the project is profitable.

$$\begin{aligned} \text{ROI} &= \frac{\text{annual profit}}{\text{total capital investment}} \times 100\% = \frac{\text{annual revenue - annual production costs}}{\text{total capital investment}} \times 100\% \\ &= \frac{\text{US\$5,227,200.00 - US\$2,728,478.18}}{\text{US\$10,442,538.22}} \times 100\% \\ &= 23.93\% \end{aligned}$$

8.3.14 Payback Period

The payback period for the investment was calculated to get the maximum period for a viable project based on a discount rate of 14% and a project life of 10years.

$$\text{Payback period of investment} = \sum_{i=1}^{10} \frac{1}{(1+r)^i} = 4.946 \text{ years}$$

r is the discount rate. The results indicate that a payback period below 4.946 years would be viable for this project provided other economic factors like the IRR are also satisfactory.

8.3.15 Internal Rate of Return

This is also called the discounted cash flow (DCF) rate of return and it is one of the best ways to evaluate a project. The calculation uses trial and error to find a discount rate at which all discounted negative and positive cash flows are equal, it can be tedious without a computer, hence a robust excel spreadsheet was used. The spreadsheet is shown in Appendix J.

8.3.16 Sensitivity Analysis

A sensitivity analysis was carried out to investigate the effect of possible changes in forecast data on the viability of the project. The major factors of interest were:

- The selling price of BPAC
- The total capital investment
- The total production costs
- The cost of bagasse

It was important to evaluate the effect of bagasse price taking into consideration that some mills in South Africa have it in excess and would be willing to dispose it cheaply if not for free because they are facing disposal problems (for example, Amatikulu and Komati Mills) while on the other hand mills like Sezela are already using bagasse for furfural production. The results of the sensitivity analysis are shown in Table 8-9 and Figure 8-3. The table shows the variation of the above factors over the range +/-20% in 10% intervals.

Table 8-9 Sensitivity analysis of IRR, ROI and Investment payback period to various factors

Economic Factors	Variation %	Amount US$	IRR %	ROI %	Payback period years
Capital investment	20%	12,5m	13.54	19.94	4.59
	10%	11,4m	15.57	21.75	4.17
	0%	10,4m	17.93	23.93	3.80
	-10%	9,4m	20.72	26.59	3.33
	-20%	8,4m	24.1	29.91	2.92
BPAC selling price (per kg)	20%	2.16	28	33.86	2.52
	10%	1.98	23.08	28.89	3.03
	0%	1.80	17.93	23.93	3.80
	-10%	1.62	12.42	18.96	4.85
	-20%	1.44	6.31	14	6.72
Production costs	20%	3,3m	12.11	18.7	4.92
	10%	3,0m	15.08	21.32	4.26
	0%	2,7m	17.93	23.93	3.80
	-10%	2,5m	20.67	26.54	3.34
	-20%	2,2m	23.34	29.15	3.00
Bagasse costs (per tonne)	20%	14.80	15.64	21.82	4.16
	10%	13.56	16.8	22.88	3.94
	0%	12.33	17.93	23.93	3.80
	-10%	11.10	19.04	24.98	3.58
	-20%	9.86	20.15	26.04	3.41
Free bagasse	Possible benefits of process integration within a sugar mill		28.59	34.47	2.47
Free bagasse, water, electricity and steam			32.12	38.15	2.19

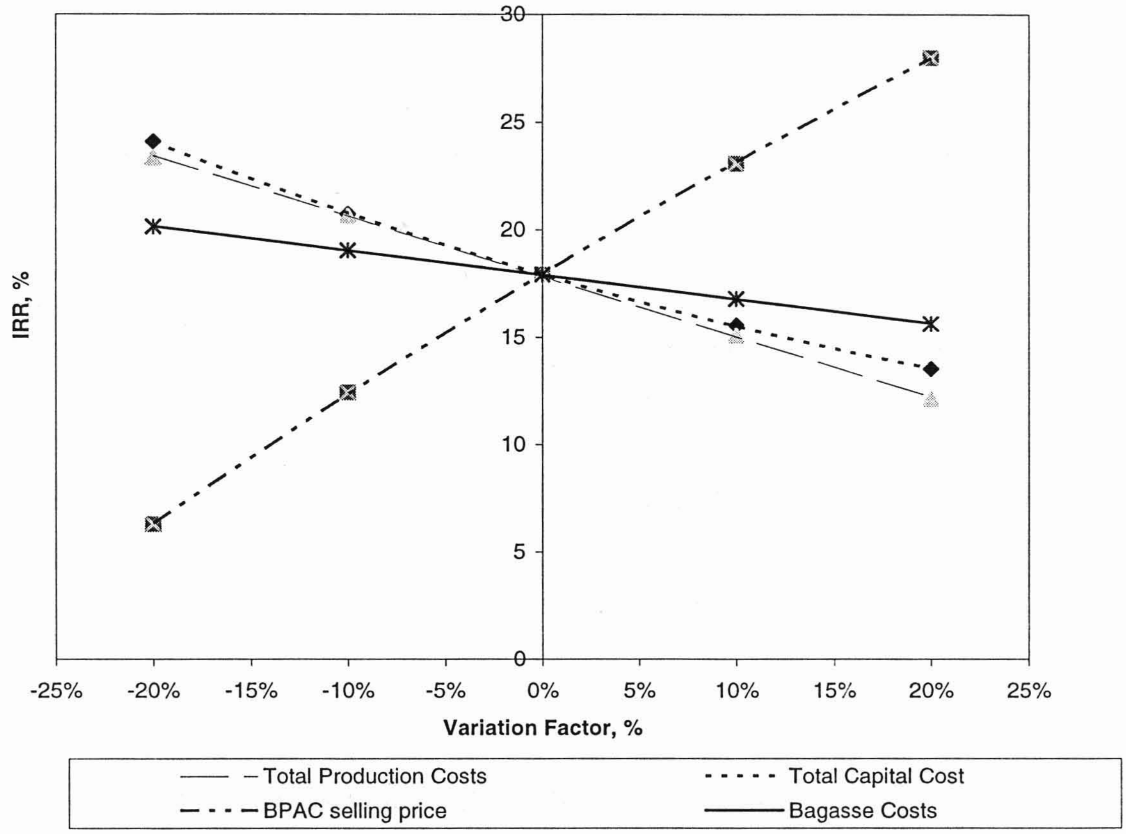

Figure 8-3 IRR sensitivity analysis of the BPAC project to various factors

From the chart, 0% represented the base IRR percentage corresponding to the original forecast data and analysis. This corresponds to a BPAC selling price of US$1.80 per kg and a bagasse costs price of US$12.33 per ton (based on coal price of US$46.85/t sourced from Business Report dated 13September, 2005).

The impact of variation in selling price and production rate on IRR, ROI and the investmnet payback period were the same since BPAC sales constitutes about 99.2% of total revenue received. An increase in selling price of BPAC by 10% to US$1.98/kg yields about 10% increase in IRR to 23.08%, and the corresponding ROI and Payback period is 28.89% and 3.03 years respectively. A decrease in selling price to US$1.62/kg is not as viable with an IRR of 12.42%, ROI of 18.96% and investment payback period of 4.85. This illustrates the sensitive nature of IRR to variation factors unlike ROI and Investment Payback for assessing viability of a project.

The influence of variability in bagasse costs is not as steep as the selling price of BPAC. However it's still important to note that a 20% decrease in bagasse price to US$9.86/t would increase the IRR by 2.22% to 20.15%, a ROI of 26.04% and a investment payback period of

3.41 years. In the event that bagasse is sourced for free, the IRR would increase to 28.59%, ROI of 34.47% and an investmnet payback period of only 2.47 years. This is an excellent result if this plant could be sited at sugar mills like Amatikulu and Komati where disposal of surplus bagasse is an environmental problem. However in the event that bagasse increases in value by 20% due to unforeseeable demand, the IRR would be 15.64%, ROI of 21.82 and investment payback period of 4.16 years.

The effect of variation of the total capital cost and production costs were not as steep as the selling price of BPAC. However the project loses its economic viability in the variation range of 10 to 20% in capital investment to yield an IRR of 15.57% and 13.54% respectively. A decrease in the capital costs results in an improvement in the IRR, ROI and investment payback period. Buying second hand equipment could help lower the costs of investment and later upgrade the equipment from sales revenue. This might be a feasible option in view of the difficult period the sugar industry of South Africa is going through due to shrinking sugar markets and low sugar prices. The total production costs follow the same trend as the capital costs, and the project loses its viability in the variation range of 10 to 20% of the production costs.

8.4 Environmental Impact Assessment (EIA) of the BPAC process

Life cycle assessment is fast becoming the common tool for assessing environmental impacts in process selection, design and optimization. There are a number of techniques available for environmental assessment and these include:

1. environmental impact assessment
2. Best practicable environmental option assessment
3. environmental impact indices
4. environmental risk assessment
5. cost-benefit analysis

The main limitation of the present practice of choosing the Best Practicable Environmental Option (BPEO) is that it tends to reduce impacts directly from the plant, but increasing them elsewhere in the life cycle. The main characteristics of above EIA options are discussed by Burgess and Brennan (2000). The main reason why the life cycle assessment method is gaining popularity is because of its ability to quantify the environmental interventions and evaluate improvement options through the life cycle of a process, product or activity and also that it uses a functional unit, e.g. Global warming: Kg -CO_2 Equiv per kg of product produced (Azapagic, 1999; Olsen *et al* 2001, Bayer *et al* 2005).

8.4.1 Life Cycle Assessment (LCA)

The Society for Environmental Toxicology and Chemistry (SETAC) defines LCA as "a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and waste released to the environment; and to identify and evaluate opportunities to effect environmental improvements". In other words LCA serves as a tool for managing the environment. According to Azapagic (1999) LCA has been applied as a decision making tool in some industrial sectors such as energy, transport, chemical, nuclear, metal, polymer, paper and forest, textile and leather, water and electronics.

8.4.2 Life cycle assessment of the BPAC manufacturing process

The LCA methodology was used to assess the environmental impacts for the manufacture of activated carbon from bagasse in order to get the best environmental friendly process. The two process options under investigation are shown in the figure above. The LCA was carried out in four phases:

1. Goal definition and scoping
2. inventory analysis
3. Impact assessment
4. improvements assessments

The goal of the study was to evaluate environment impact of the activated carbon manufacturing process using a functional unit of kg of BPAC. The second stage involved quantifying environmental burdens in terms of resource depletion and emissions etc using a mass and energy balance. The burdens were then classified into impact categories like global warming etc and finally characterized by quantifying the different potential-impact categories. Unlike the usual 'cradle to grave' analysis for full life cycles, a 'cradle to gate' approach was used for comparing the different process options. A software tool called GaBi3 was used to model the different process options with the aid of its updated databases, models for calculations and visualization of material and energy flow systems. The impacts were estimated per unit mass for the following categories:

- global warming (kg CO_2 Equiv) – indicates potential of emissions to cause global warming compared to carbon dioxide over a time period of 20years, 50years or 100 years
- Acidification (kg SO_2 Equiv) – indicates acidic emissions
- Eutrophication (kg PO_4^- Equiv) – indicates the adverse growth of aquatic biomass due to nutrient enrichment
- Ozone depletion (kg ethane Equiv) – indicates ozone depletion compared to ethene
- Aquatic Toxicity (kg DCB Equiv) - indicates potential risk to affect aquatic life

- Terrestrial Toxicity (kg phosphates Equiv) – indicates adverse effects to ecosystem as a result of nutrient enrichment to the soils compared to phosphates
- Human Toxicity (kg DCB Equiv) – indicates potential risk to cause cancer

8.4.3 Sustainability of the BPAC manufacturing process

The relationship between the sugar mill and the BPAC plant where the waste from one manufacturing process is taken to another industry to be used as a raw material is termed industrial ecology. Figure 8-4 illustrates the development of the activated carbon life cycle map, which depicts the sequence of activities associated with active carbon, from sugarcane production through extraction to final disposal of spent BPAC.

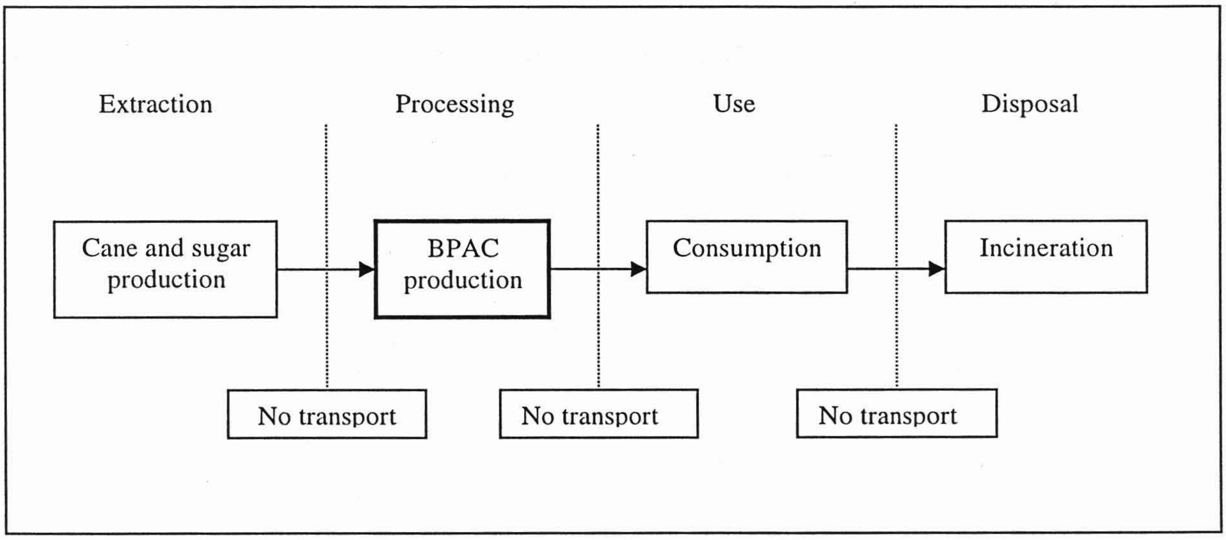

Figure 8-4 The proposed scheme for sustainable active carbon production and utilization

8.4.4 BPAC process description

The commercial plant design is based on results generated during investigation on screening, drying, pyrolysis and activation of bagasse, and the decolourising effect of BPAC on clear juice. The theoretical significance of each processing unit is discussed in detail in Chapter 4 and 5. The conceptual design for the demonstration plant incorporates recovery cycles for both sensible heat and calorific value of the combustibles to satisfy the process thermal energy requirements. This minimizes the total electrical energy requirements to the BPAC process from the mill. Two options shown in Figure 8-5 and Figure 8-6 were compared based on the available conceptual designs developed for manufacture of activated carbon from bagasse.

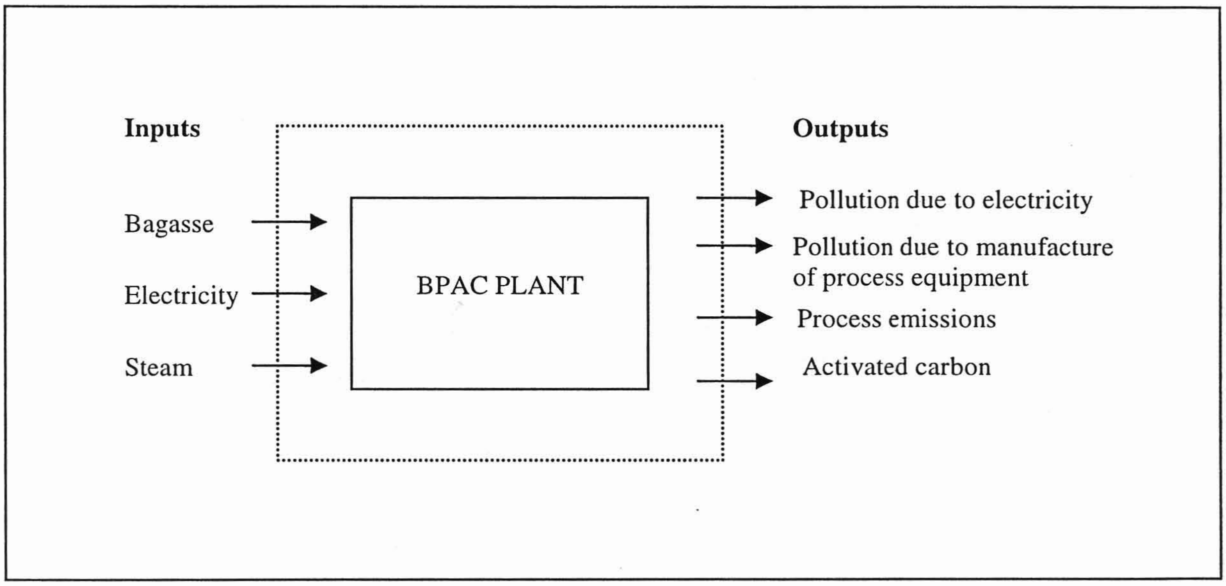

Figure 8-5 Option 1 - Active carbon production system (Developed from a conceptual process design by Devnarain, 2003)

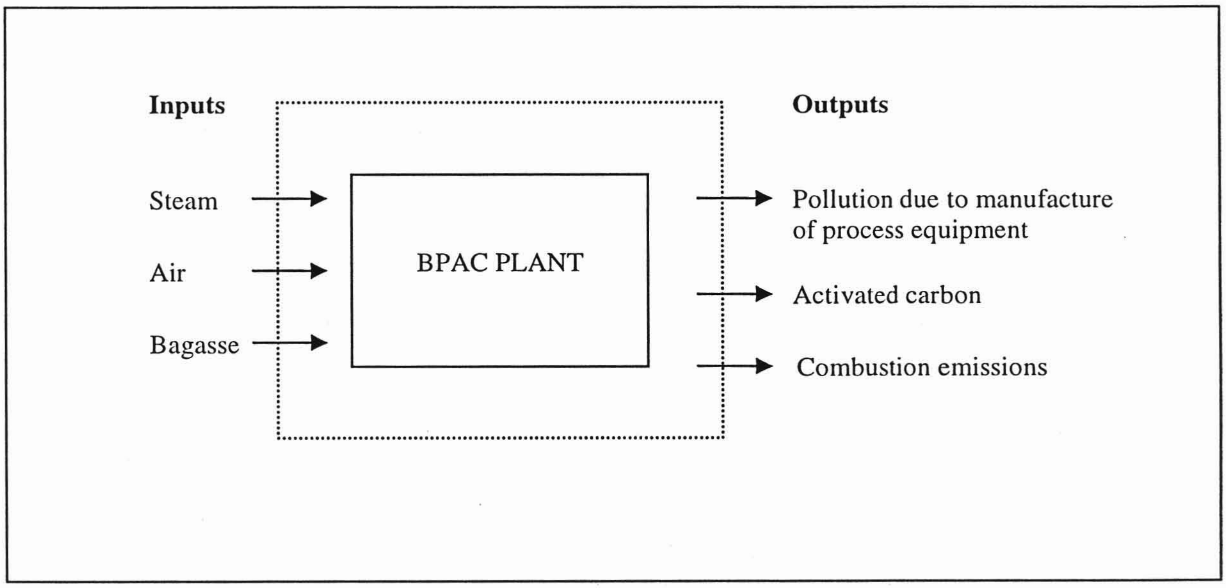

Figure 8-6 Option 2 - Active carbon production system with recovery of combustibles (conceptual design from this study)

8.4.5 Impact Assessment according to the Gabi 3 Model

There are a number of life cycle analysis software tools available such as Simapro, GABI, Umberto, and EcoScan. According to Institute for Polymer Testing and Polymer Science (IKP) at the University of Stuttgart GaBi 3 is the only software in the world to give opportunity to carry out, with the help of so-called costs assistants, an exact economic examination of the system defined in the eco-balance on the basis of material/energy costs, personnel costs and machine costs.

The bagasse processing options were considered and these were modeled using the GaBi 3 tool:

1. processing bagasse for activated carbon production without energy recovery and using with power from cogeneration for thermal energy requirements
2. processing bagasse for activated carbon production with energy recovery from emissions eliminating the need to use electrical energy for thermal energy requirements

Table 8-10 Environmental profile for the BPAC process (Basis of 1kg of active carbon)

Environmental impact category	**Units**	**Option 1**	**Option 2**
Global warming potential (20 years)	Kg CO2 equiv	36.728	11.116
Acidification Potential	Kg SO2 equiv	0.013	-
Eutrofication potential	Kg PO4 equiv	0.002	-
Ozone depletion	Kg ethane equiv	6.82 E -09	-
Aquatic Toxicity	Kg DCB equiv	1.07 E -04	-
Terrestrial Toxicity	Kg DCB equiv	16.749	-
Human Toxicity	Kg DCB equiv	0.184	-

From the results in Table 8-10 the most dominating process for all environmental categories under investigation is electricity. A summary of inputs and outputs for 1MJ of energy (electricity) is shown in Appendix F. Considering a worst scenario case where there is maximum use of electrical energy (no energy recovery and reuse) the results are shown as option 1. Option 2 shows excellent results in most environmental categories and the main influence was the incineration of combustibles (CO, H_2, CH_4, C_2H_4, $C_{10}H_4$ or tar, etc) and reuse of energy streams to minimise use of electricity. For comparison sake, electrical energy requirements for moving equipment and other small jobs were common in both and hence not considered; this effectively means Option 2 has zero energy input. Without electrical energy, Global warming was the only impact with a rating of 11.116 against Option 1 with a higher rating of 36.728 kg CO2 equiv per kg of active carbon produced.

The high GWP rating of 11.116 kg CO_2 per kg of BPAC is attributed to the high carbon burn-off (about 68%) during steam activation and denotes the high loss of carbon during processing.

CONCLUSIONS AND RECOMMENDATIONS

Based on the on experimental and derived results, and discussion, the following conclusions can be drawn:

1. Activated carbon can be made from untreated sugarcane bagasse in a rotary batch kiln.
2. The quality of the activated carbon is dependent on the operating conditions which include peak temperature, residence time, steam partial pressure and steam to feed ratio.
3. The best activated carbon prepared had an MBN of 257mg/g of BPAC at a corresponding activated carbon yield of 7 wt% on bagasse. The best operating conditions were pyrolysis at 700°C for a hold time of 1hour and activation at 850°C for an activation time of 1hour. Pure steam was used as the activating agent at a rate of 5g/min.
4. The combustible gases had a total calorific value of about 94MJ/kg of activated carbon made. In addition the off-gases were at temperatures above 700°C with a total sensible heat of about 46MJ/kg of activated carbon. From mass and energy balances, this energy was enough to satisfy the thermal energy requirements of the drying, pyrolysis and activation processes.
5. The adsorptive capacity of BPAC increased with brix up to a maximum of 22.7% at 39°Brix while the optimum concentration for Norit PN2 was 33.5° Brix with a colour removal of 12.3%.
6. Activated carbon requirements for a factory operating at a clear juice (12°Brix) flowrate of 600m^3/h were about 500kg/h at a dosage rate of 0.7wt% of BPAC on brix.
7. The total capital investment for a demonstration plant sited on a sugar mill was estimated at about US$10.4 million with IRR, ROI and Investment payback period of 17.93%, 23.93% and 3.8 years respectively at BPAC selling price of US$1.80
8. A sensitivity analysis was carried out to investigate the possible effect of variation in BPAC selling price, bagasse buying price, capital investment and production costs on IRR, ROI and payback time. Free bagasse and plant utilities would be additional bonus to the project feasibility.
9. The environmental impact of the demonstration plant was mainly global warming, with a rating of about 11kg CO_2 equivalent illustrating the benefits of energy recovery and reuse.

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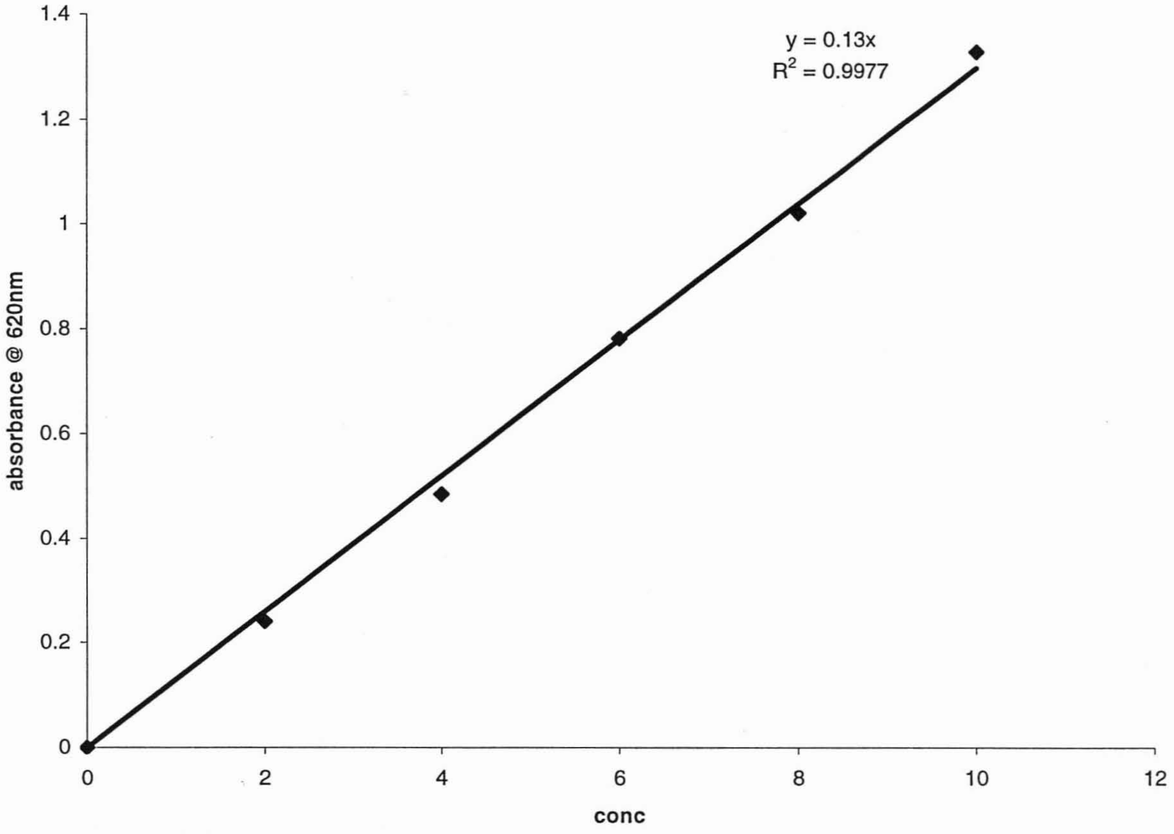
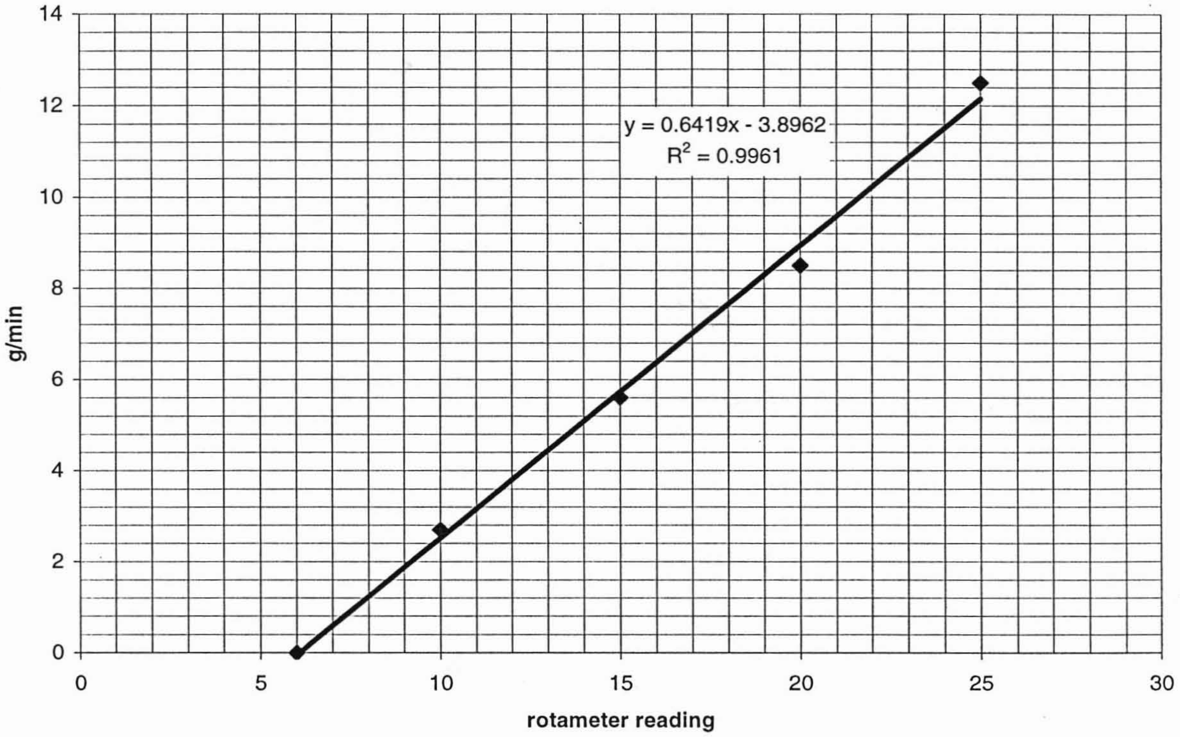
Appendix A

Calibration curve for Methylene Blue

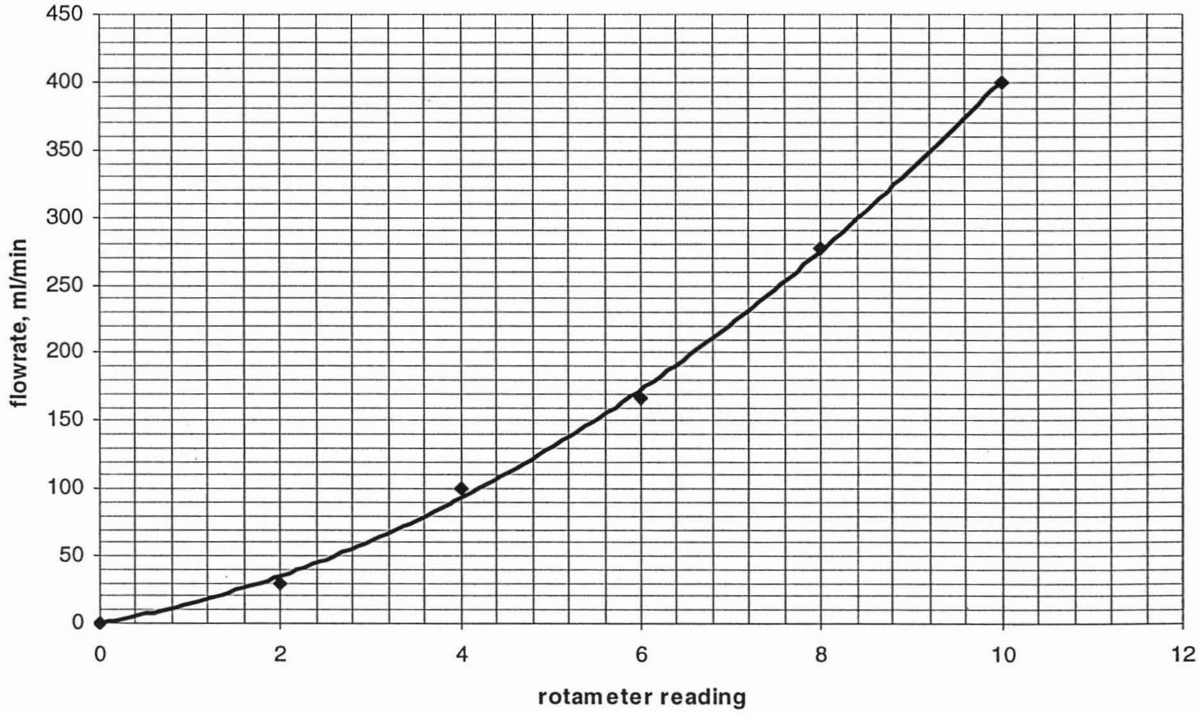


Appendix B

Steam Calibration Curve



Nitrogen Calibration Curve



Appendix C

Mass and Energy Balance

General Input Data

Type of waste:	Bagasse	
Feedrate	42.75	t/h, wet
CV	8.00	GJ/t, wet
	15.40	GJ/t, dry
Cp	0.0013	GJ/t.°C, dry
	0.0028	GJ/t. deg C, wet
moisture content, %wt as rec	49%	wt basis
bagasse feed temperature	25	deg cels

Screening	coarse fr	62%	wt basis as received
Drying	final temperature	200	°C
	heat loss	0	GJ/h
Pyrolysis	rate of heating	10	°C/min
	peak temperature	700	°C
Activation products	active carbon	35%	dry basis on char
	steam temperature	150	°C

		mass%	
Pyrolysis products	charcoal	22%	
	tar	10%	
	aqeous phase	43%	
	gas	25%	(by difference)
	Total	100%	

Gaseous Fuel Composition (vol %)	Pyrolysis	activation
H2	0.06	-
CO	23.40	20.4
CH4	4.66	21.7
CO2	71.63	57.9
C2H4	0.26	-
C2H6	traces	-
	100.0	100.0

Screening

Mass balance			
inputs	wet bagasse	t/h	42.8
outputs	wet coarse fraction:	t/h	26.5
	wet fine fraction:	t/h	16.2

Drying

feed	wet bagasse	t/h	26.5		212.0
products	dry bagasse	t/h	13.0		
	water vapour	t/h	13.5		

		t/h	temp deg C	potential GJ/h	enthalpy >25C
input	dry bagasse	13.0	25.0	200.0	0.0
	moisture	13.5	25.0	-	0.0
				200.0	0.0
outputs	dry bagasse	13.0	200.0	200.0	3.0
	water vapour	13.5	200.0	-	35.7
				200.0	38.6

Pyrolysis

feed	dry bagasse	t/h	13.0
products	gases	t/h	3.2
	tar	t/h	1.3
	aqeous phse	t/h	5.6
	char	t/h	2.9

Pyrolysis products

	% v/v	density kg/m^3	Nm^3/h	volume MJ/Nm^3	CV GJ/h
H_2	0.06	0.09	1.12	10.79	0.01
CO	23.40	1.25	437.94	12.61	5.52
CH_4	4.66	0.71	87.21	35.82	3.12
CO_2	71.63	1.96	1340.59		0.00
C_2H_4	0.26	1.25	4.87	59.51	0.29
C_2H_6	traces	1.34			
average density					8.95

*density under normal conditions (273.15K; 101.325kPa)

		t/h	Nm^3/h	temp deg C	potential GJ/h	Hrxn GJ/h	enthalpy >25C
input	dry bagasse	12.99		200.00	200.02	-8.57	2.95
output	char	2.86		700.00	85.72		3.28
	H2	0.0001	1.12	700.00	0.01		0.00
	CO	0.55	437.94	700.00	5.52		0.41
	CH4	0.06	87.21	700.00	3.12		0.14
	CO2	2.63	1340.59	700.00	0.00		1.92
	C2H4	0.01	4.87	700.00	0.29		0.01
	tar	1.30		700.00	53.34		2.51
	aqeous	5.58		700.00	-		5.20
	total	12.99			148.01		13.47

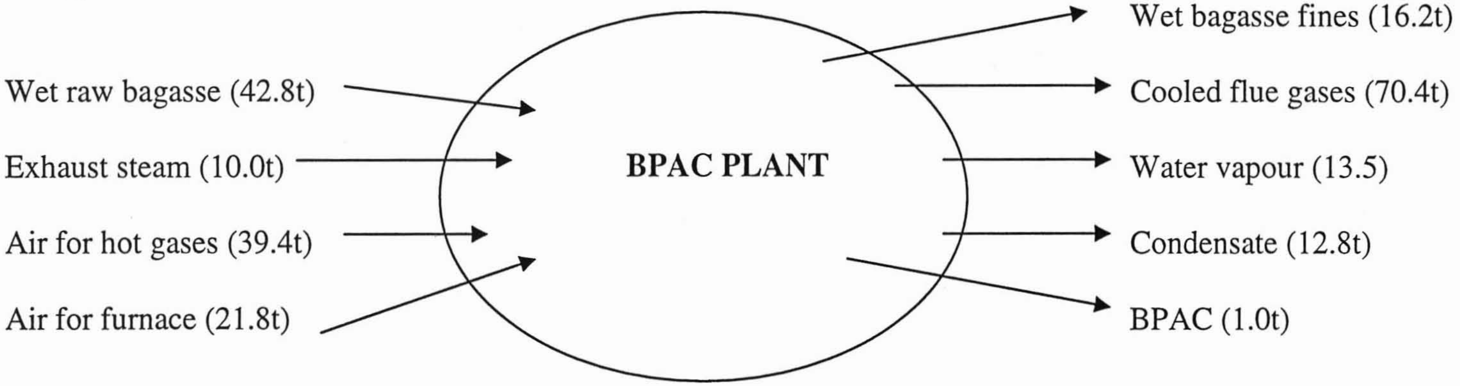
Activation

inputs	char	t/h	2.86		
	steam	t/h	10.00		
outputs	gases	t/h	4.64	3002.16	Nm^3
	steam	t/h	7.21		
	active carbon	t/h	1.00		

gaseous products	% v/v mf	density kg/Nm^3		volume Nm^3/h	CV MJ/Nm^3	Potential energy GJ/h
CO	20.39	1.25	0.25	612.14	12.61	7.72
CO2	57.93	1.96	1.14	1739.15	0.00	0.00
CH4	21.68	0.71	0.15	650.87	35.82	23.31
average density			1.55			31.03

		t/h	Nm^3/h	temp deg C	potential GJ/h	Hrxn GJ/h	enthalpy >25C
input	char	2.86		700	85.72	20.99	3.28
	steam	10.00		150			1.98
		12.86			85.72	20.99	5.26
output	active carbon	1.00		850	31.00		1.40
	CO	0.76	612.14	850	7.72		0.71
	CO2	3.41	1739.15	850	0.00		3.12
	CH4	0.46	650.87	850	23.31		1.37
	steam	7.21		850			12.50
		12.86			62.04		19.10

Overall mass balance



Appendix D

Sugar decolourisation tests - short communication

Determination of colour in sugar solutions

The standard ICUMSA colour test method 5 was used for colour analysis of sugar solutions.

Reagents

Hydrochloric acid 0.05 M

Sodium Hydroxide 0.05 M

Apparatus

Spectrophotometer

Optical glass cells – 10 mm

Membrane filters – cellulose nitrate filters with a pore size 0.45 µm and 50 mm ϕ.

Buchner funnel – porcelain (50–65 mm ϕ)

Buchner flask – 500 cm^3 capacity with rubber bung to fit flask

pH meter

Refractometer

Magnetic stirrer with follower

Laboratory balance

Beakers – 250 cm^3, 100 cm^3, 50 cm^3

D.1. Determining colour of raw sugar solutions

- The sample of sugar was mixed thoroughly.
- 30 ± 0.02 g of raw sugar was weighed into a 250 cm^3 beaker.
- 70 cm^3 of distilled water was added.
- A magnetic stirrer and stirrer bar was used to dissolve the sugar.
- The solution was then filtered through a 0.45 µm membrane under vacuum into a dry Buchner flask.
- The solution was then transferred to a 50 cm^3 beaker.
- The pH was adjusted to 7 ± 0.02 using HCl and NaOH (both of 0.05M) with continuous stirring.
- The absorbance of the solution was measured on a spectrophotometer in a 10 mm cell using distilled water as a reference.
- The Bx of the solution was measured using a bench refractometer and the colour was calculated.

D.2. Determination of the colour of syrup

- Procedure
- The sample was mixed thoroughly.
- A solution of approximately 5°Bx was prepared by dissolving 7 g of syrup in distilled water to a total volume of 100 cm^3.
- The solution was mixed on a magnetic stirrer with a stirrer bar and divided into two portions.
- One portion was filtered through a membrane filter under vacuum.

- Both samples were adjusted to pH 7 ± 0.02 and their absorbencies were read on the spectrophotometer at 420 nm using a 10 mm cell.
- The brix of the solution was read and their colour.

D.3. Determination of the colour of clear juice

- The brix of the juice was determined.
- A 5°Bx solution of juice was prepared by diluting a calculated mass of juice to 100ml according to the following:

$$mass\ of\ \ juice = \frac{100}{Brix} \times \frac{5}{1}$$

- The calculated mass of juice was weighed out in a beaker and made up to 100 ± 0.02 g with distilled water.
- Thereafter the solution was stirred well and filtered.
- The pH of the solution was adjusted to 7 ± 0.02 and its absorbance was read using a 1 cm cell at 420nm. The colour of the original solution was calculated in terms of absorbance units per unit of brix.

Using the data for the blank sample before heating:

$$\begin{aligned} ICUMSA\ 420\ colour &= \frac{A_s * 10000}{b(c/100)} \\ &= \frac{1.806 * 10000}{\left(\frac{50 * 30.17}{100}\right)} \\ &= 1197 \end{aligned}$$

Using the data for Norit PN2 at 0.5% dosage:

$$\begin{aligned} \%\ Decolourisation &= \frac{colour\ of\ \ blank\ heated - colour\ of\ \ sample\ with\ carbon\ heated}{colour\ of\ \ blank\ heated} \times 100\% \\ &= \frac{1967 - 572}{1967} * 100 \\ &= 71\% \end{aligned}$$

D.4. Decolouring effect of PAC on brown liquor

- 80 g of brown liquor at 65°Bx was dosed with a specified loading of PAC (m/m EBx).
- The sample was heated at 80°C, with constant stirring for 24 hours in a massecuite mixer.
- A blank sample (without PAC) was subjected to the same conditions.

Carbon used	% CARBON	Absorbance	Brix	g sucrose/100cm^3	ICUMSA COLOUR	% Colour removal
BPAC	Blank1 - Before heating	1.806	27	30.17	1197	
	Blank2 - After heating	0.736	33	37.408	1967	
	0.5	0.232	34	38.976	595	70
	1	0.438	30	34.318	255	87
	1.5	0.294	37	42.966	137	93
	2	0.266	31	34.701	153	92
Norit PN2	Blank1 - Before heating	1.806	27	30.17	1197	
	Blank2 - After heating	0.736	33	37.408	1967	
	0.5	0.999	31	34.957	572	71
	1	0.453	25	27.345	331	83
	1.5	0.254	35	39.898	127	94
	2	0.158	28	31.29	101	95
	5	0.069	31	33.937	41	98
	Blank1 - Before heating	1.806	27	30.17	1197	
	Blank2 - After heating	0.649	31	35.085	1850	
PCX	0.5	0.074	37	42.966	172	91
	1	0.048	29	32.797	146	92
	1.5	0.018	21	23.03	78	96
	2	0.031	38	43.641	71	96
P9-45	0.5	0.41	39	45.408	903	51
	1	0.276	43	51.256	538	71
	1.5	0.147	38	44.454	331	82
	2	0.104	37	42.831	243	87

D.5. Effect of Brix on the Efficiency of PAC Decolourisation

- Clear juice was evaporated by means of a rotating evaporator (rotavap) under vacuum to various brix levels.
- BPAC and PN2 were added to the concentrated solutions at a dosage of 0.5% (m/m EBx).
- The solutions were then heated in the massecuite mixer for 1 hour at 80 °C.
- A blank sample was included for each brix tested.

SAMPLE	BRIX OF SAMPLE	ABSORBANCE	BRIX OF DILUTED SAMPLE	g Sucrose per 100 cm^3	ICUMSA COLOUR	% COLOUR REMOVAL
BPAC						
1	13	1.198	4.6	4.675	25626	16.8
3	20	0.738	4.3	4.365	16907	18.1
5	31	0.734	4.7	4.778	15362	21.9
7	39	0.716	4.5	4.571	15664	22.7
9	52	0.855	5.4	5.506	15529	21.8
11	62	0.413	2.6	2.622	15751	20.7
PN2						
1	11.5	1.129	4.6	4.675	24149.7	8.5
3	18.4	0.943	4.2	4.262	22125.8	11.5
5	33.5	0.95	4.3	4.365	21764	12.3
7	47	0.93	4.3	4.365	21305.8	10.7
9	56	0.627	2.8	2.826	22186.8	10.4

D.6. Effect of Residence Time on PAC Decolourisation

- Clear juice (12 °Bx) dosed with 0.5% PAC (m/m EBx) was heated at 80°C for various time increments with continuous stirring in a massecuite mixer.
- For each time increment a blank sample was also subjected to the same conditions.
- The brix was kept constant since no evaporation took place.

	BLANK						SAMPLE + CARBON				
Carbon Used	TIME	%Carbon	Absorbance	Brix	g sucrose/ $100cm^3$	ICUMSA COLOUR	Absorbance	Brix	g sucrose/ $100cm^3$	ICUMSA COLOUR	% Colour removal
PN2	0	0	1.354	4.5	4.571	29622					
	10	0.5	1.948	5.8	5.922	32894	1.605	5	5.089	31539	4
	30	0.5	1.832	5.2	5.297	34586	1.297	3.8	3.85	33688	3
	60	0.5	1.46	4.6	4.675	31230	1.204	4.2	4.262	28250	10
	120	0.5	1.818	4.8	4.882	37239	1.05	3.6	3.644	28814	23
	240	0.5	1.694	5	5.089	33287	1.251	4.2	4.262	29352	12
BPAC	0	0	1.41	4.8	4.882	28882					
	10	0.5	1.982	5.1	5.193	38167	1.701	4.5	4.571	37213	2
	30	0.5	1.889	5	5.089	37119	1.489	4.6	4.675	31850	14
	60	0.5	1.38	4.4	4.468	30886	1.162	5.0	5.089	22834	26
	120	0.5	1.792	5	5.089	35213	0.991	4.6	4.675	21198	40
	240	0.5	1.653	4.7	4.778	34596	1.002	5.1	5.193	19295	44

D.7. Determination of the optimum quantity of PAC required for decolourisation

- Clear juice at 12° brix was dosed with varying quantities (m/m EBx) of BPAC and PN2.
- The samples were heated under vacuum in a rotary evaporator and evaporated until a brix of 65° was obtained. The evaporation process took 1 hour.
- The ICUMSA colour of the final syrup was determined.
- A blank sample without carbon was subjected to the same process.
- The temperature range at which the experiment was carried out was 65°C.

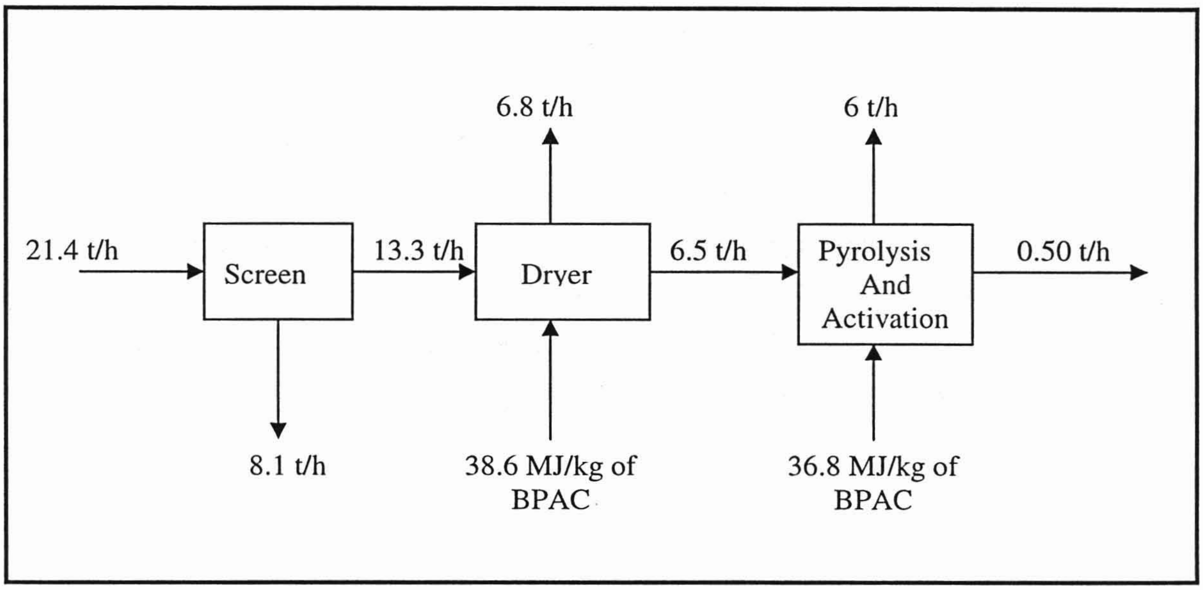
	% Carbon	Absorbance	Brix	g sucrose/100cm3	ICUMSA colour	% Colour removal
PN2	0	1.341	4.8	4.882	27468	0
	0.1	1.382	4.8	4.882	28308	-3
	0.5	0.953	3.8	3.85	24753	10
	1	0.689	3.1	3.132	21999	20
	2	0.421	2.7	2.724	15455	44
	5	0.451	4.4	4.468	10094	63
	10	0.171	5.7	5.818	2939	89
BPAC	0	1.267	4.8	4.882	25952	0
	0.5	0.824	3.7	3.747	21991	15
	0.75	0.798	4	4.056	19675	24
	1	0.873	5.2	5.297	16481	36
	2	0.347	3.4	3.439	10090	61
	5	0.09	3.4	3.439	2617	90

D.8 Adsorption isotherm spreadsheet

Carbon used	% CARBON	Absorbance	Brix	g sucrose/100cm^3	ICUMSA COLOUR	% Colour removal	Freundlich isotherms		Langmuir isotherms	
BPAC	Blank1 - Before heating	1.806	27	30.17	1197					
	Blank2 - After heating	0.736	33	37.408	1967		Log (x/m)	Log (Ce)	Ce/x/m)	Ce
	0.5	0.232	34	38.976	595	70	2.15	2.77	4.25	595
	1	0.438	30	34.318	255	87	1.94	2.41	2.93	255
	1.5	0.294	37	42.966	137	93	1.79	2.14	2.21	137
	2	0.266	31	34.701	153	92	1.66	2.18	3.33	153
Norit PN2	Blank1 - Before heating	1.806	27	30.17	1197					
	Blank2 - After heating	0.736	33	37.408	1967					
	0.5	0.999	31	34.957	572	71	2.15	2.76	4.03	572
	1	0.453	25	27.345	331	83	1.92	2.52	3.99	331
	1.5	0.254	35	39.898	127	94	1.80	2.10	2.03	127
	2	0.158	28	31.29	101	95	1.68	2.00	2.13	101
	5	0.069	31	33.937	41	98	1.29	1.61	2.09	41
	Blank1 - Before heating	1.806	27	30.17	1197					
	Blank2 - After heating	0.649	31	35.085	1850					
PCX	0.5	0.074	37	42.966	172	91	2.26	2.24	0.95	172
	1	0.048	29	32.797	146	92	1.96	2.16	1.59	146
	1.5	0.018	21	23.03	78	96	1.81	1.89	1.22	78
	2	0.031	38	43.641	71	96	1.68	1.85	1.48	71
P9-45	0.5	0.41	39	45.408	903	51	2.01	2.96	8.85	903
	1	0.276	43	51.256	538	71	1.85	2.73	7.58	538
	1.5	0.147	38	44.454	331	82	1.74	2.52	6.05	331
	2	0.104	37	42.831	243	87	1.64	2.39	5.59	243

Appendix E

Equipment Sizing and Costing



Costing the rotary trommel

The cost of the screen is based in the material of the screen type, surface area, material and the cloth. From experimental results a yield of 61% was considered the best separation in a rotary screen. The residence time of the bagasse was 30sec at a bagasse filling ratio of 15% by volume.

The volume of the rotary trommel = bagasse flowrate (Q) x residence time (τ)

$$= 21400/120 \times 30/3600$$

$$= 1.486\text{m}^3.$$

At 15% fill by volume, the actual volume of the screen = 1.625/0.15 = 9.907m^3.

Taking a diameter, d of 1m (and using $V = \pi d^2 L/4$) the length, L of the trammel = 12.6m

This translate to a screen area of the rotary trommel = πdL = 39.6m^2.

From the Match Co, the cost of carbon steel rotary trommel with a screen made from light carbon steel wire = **US$ 50, 000.00**

Costing the dryer

The cost of a dryer is based on the type of dryer, heat transfer surface area, material used and the nature of the contents (low hazard, corrosive, etc).

The heating rate for the dryer is given by:

$$Q = UA\Delta T$$

Q = heat load (W), U = Overall heat transfer rate (W/m^2.K), A = Area of dryer (m^2) and ΔT = temperature differential across the wall, K

Using an overall heat transfer of steel of 25W/m^2.K, the area of the dryer is given by:

$$A = \frac{Q}{U\Delta T} = \frac{\left[{(38.6 \times 500} \big/ {3600} \right] \times 10^6}{25(700 - 237)} = 463 m^2$$

From the Match Co, the cost of an indirect fired rotary dryer = **US$ 1.14m**

Costing a rotary kiln for pyrolysis and activation

The cost of a kiln is based on the type of kiln and the heating duty.

From the energy balance, the total thermal energy required for pyrolysis and activation is about 36.8 MJ/kg of BPAC. Considering a BPAC production rate of 500 kg/h and an energy efficiency of 80%, the total thermal energy requirements = 23 GJ

From the Match Co, the cost of a large indirect fired rotary kiln made from carbon steel for the above heating duty = **US$ 2.3m**

Appendix F

Determining Environmental Impact using GABI-3

Summary of Inputs and Outputs for thermal electricity – Basis of 1MJ of energy

Inputs

Primary energy from hydro power (BUWAL) [Renewable energy resources]	Energy (net calorific value)	0.0019407 MJ
Wood (BUWAL) [Renewable energy resources]	Mass	0.063099 kg
Raw brown coal (BUWAL) [Lignite (resource)]	Mass	3.2023E-6 kg
Crude oil free wellhead [Crude oil (resource)]	Mass	2.716E-5 kg
Raw hard coal (BUWAL) [Hard coal (resource)]	Mass	2.7556E-6 kg
Uranium free ore (BUWAL) [Uranium (resource)]	Mass	8.9051E-8 kg
Raw natural gas (BUWAL) [Natural gas (resource)]	Mass	4.5112E-6 kg

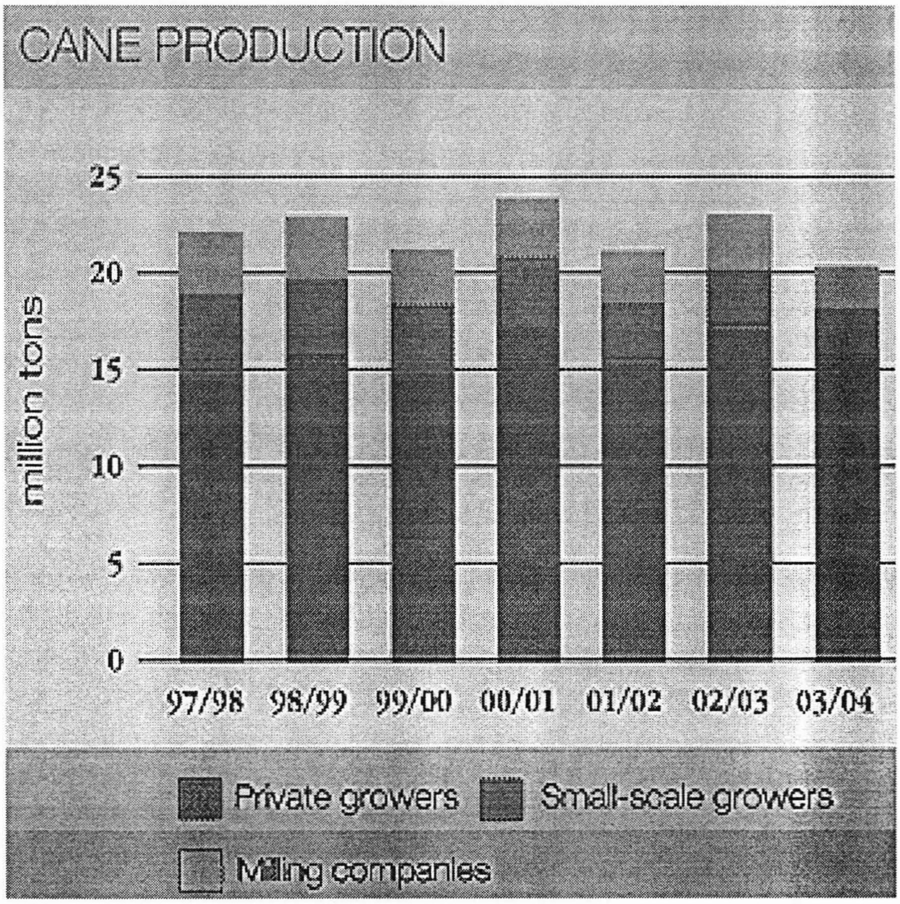
Outputs

Thermal energy (MJ) [Thermal energy]	Energy (net calorific value)	1 MJ
Carbon dioxide [Inorganic emissions to air]	Mass	0.00017908 kg
Carbon monoxide [Inorganic emissions to air]	Mass	0.0006876 kg
Methane [Organic emissions to air (group VOC)]	Mass	4.3627E-6 kg
Nitrous oxide (laughing gas) [Inorganic emissions to air]	Mass	6.7632E-7 kg
NMVOC (unspecified) [Group NMVOC to air]	Mass	5.7779E-6 kg
Nitrogen oxides [Inorganic emissions to air]	Mass	0.00011665 kg
Sulphur dioxide [Inorganic emissions to air]	Mass	2.4225E-5 kg
Dust (unspecified) [Particles to air]	Mass	0.00013316 kg
Hydrogen chloride [Inorganic emissions to air]	Mass	1.2218E-6 kg
Hydrogen fluoride [Inorganic emissions to air]	Mass	3.3671E-8 kg
Chlorinated hydrocarbons (unspecified) [Halogenated organic emissions to water]	Mass	1.3242E-12 kg
Lead [Heavy metals to air]	Mass	2.2653E-8 kg
Cadmium [Heavy metals to air]	Mass	5.9152E-11 kg
Manganese [Heavy metals to air]	Mass	1.8852E-7 kg
Nickel [Heavy metals to air]	Mass	3.1305E-10 kg
Mercury [Heavy metals to air]	Mass	1.7662E-12 kg
Zinc [Heavy metals to air]	Mass	2.2902E-7 kg
Ammonia [Inorganic emissions to air]	Mass	9.981E-6 kg
Benzene [Group NMVOC to air]	Mass	1.1094E-6 kg
Adsorbable organic halogen compounds (AOX) [Analytical measures to water]	Mass	3.593E-12 kg
Biological oxygen demand (BOD) [Analytical measures to water]	Mass	1.2666E-10 kg
Chemical oxygen demand (COD) [Analytical measures to water]	Mass	1.4574E-9 kg
Aromatic hydrocarbons (unspecified) [Group NMVOC to air]	Mass	6.3321E-7 kg
Total organic bounded carbon [Analytical measures to water]	Mass	1.9501E-8 kg
Arsenic [Heavy metals to water]	Mass	2.9023E-11 kg
Barium [Inorganic emissions to water]	Mass	3.907E-9 kg
Lead [Heavy metals to water]	Mass	1.5656E-9 kg
Cadmium [Heavy metals to water]	Mass	8.9243E-12 kg
Halon (1301) [Halogenated organic emissions to air]	Mass	6.4876E-12 kg
Iron [Heavy metals to water]	Mass	1.9534E-8 kg

Metals (unspecified) [Particles to air]	Mass	2.1232E-7 kg
Copper [Heavy metals to water]	Mass	4.563E-11 kg
Nickel [Heavy metals to water]	Mass	6.6273E-11 kg
Mercury [Heavy metals to water]	Mass	1.1873E-13 kg
Zinc [Heavy metals to water]	Mass	2.0883E-10 kg
Aluminum [Inorganic emissions to water]	Mass	3.293E-8 kg
Ammonium / ammonia [Inorganic emissions to water]	Mass	1.4153E-8 kg
Chloride [Inorganic emissions to water]	Mass	1.2014E-6 kg
Cyanide [Inorganic emissions to water]	Mass	6.5109E-12 kg
Nitrate [Inorganic emissions to water]	Mass	2.2736E-9 kg
Phosphate [Inorganic emissions to water]	Mass	1.3053E-9 kg
Sulphate [Inorganic emissions to water]	Mass	7.136E-6 kg
Phenol (hydroxy benzene) [Hydrocarbons to water]	Mass	1.8849E-10 kg
Toluene (methyl benzene) [Hydrocarbons to water]	Mass	1.6112E-10 kg
Chromium (unspecified) [Heavy metals to water]	Mass	1.379E-10 kg
Metals (unspecified) [Particles to water]	Mass	1.591E-8 kg
Halogenated hydrocarbons (unspecified) [Halogenated organic emissions to air]	Mass	7.4007E-12 kg
Nitrogen [Inorganic emissions to water]	Mass	2.1467E-9 kg
Sulphide [Inorganic emissions to water]	Mass	3.6966E-11 kg
Total dissolved organic bounded carbon [Analytical measures to water]	Mass	6.3324E-11 kg
Solids (suspended) [Particles to water]	Mass	3.1841E-7 kg
Oil (unspecified) [Hydrocarbons to water]	Mass	3.6087E-8 kg
Polycyclic aromatic hydrocarbons (PAH, unspec.) [Hydrocarbons to water]	Mass	1.7693E-11 kg
Nitrogen organic bounded [Inorganic emissions to water]	Mass	1.3624E-10 kg
Radioactive substances (unspecified) [Radioactive emissions to air]	Activity	7.8678 Bq
Inorganic salts and acids (unspecified) [Inorganic emissions to water]	Mass	7.8508E-7 kg
Radioactive substances (unspecified) [Radioactive emissions to water]	Activity	0.070331 Bq
Aromatic hydrocarbons (unspecified) [Hydrocarbons to water]	Mass	1.1626E-9 kg
Polycyclic aromatic hydrocarbons (PAH) [Group PAH to air]	Mass	6.6861E-10 kg

Appendix G

Cane Production in South Africa

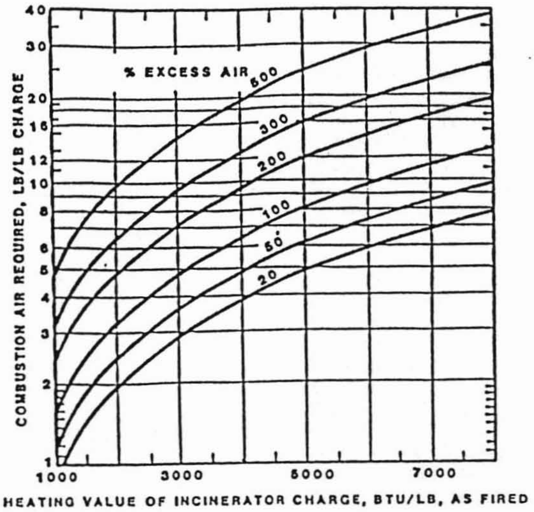


Courtesy of Illovo Sugar Industries.

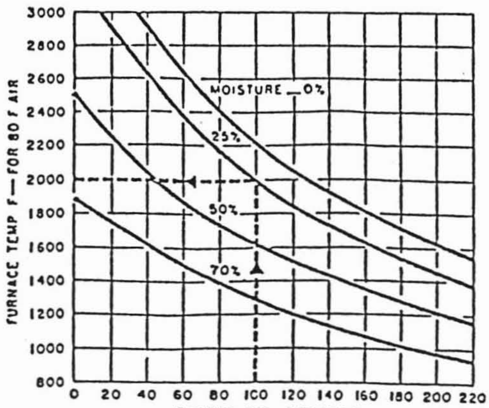
Appendix H

Calculating Furnace Air Requirements

The heating value of the charge = 94 GJ and the total mass is 9.2 t The actual combustibles are 3.1t This gives about 4400 BTU/lb of charge as fired. Using 70% excess air gives about 6.95lb/lb charge of combustibles. Therefore the amount of air required for complete combustion is about 21.8t



Using 70% excess air at a moisture content in the region below 25%, The furnace temperature read from the graph below is about 2550°F (1400°C).



Appendix I

Values of $\Delta H_{pyrolysis}$ by Different Authors

$\Delta H_{pyrolysis}{}^{a}$ (J/g)	source
−360	Bamford et al. (1946), Weatherford et al. (1965)
−220	(recalculated by Roberts (1975))
750	(recalculated by Kung (1975))
−84 to −126 (low *T*)	Tinney (1965)
−840 to −2100 (high *T*)	
−1016	(averaged by Roberts (1975))
−314 to −1700	Roberts and Clough (1963)
203	(recalculated by Kung and Kalekar (1973))
0, −210, −420	Roberts (1971)
0	Kanury (1971)
1255 to 2510	Kung (1972)
418 (low heat flux)	Lee et al. (1977)
−393 to −1090 (high heat flux)	
300	Kanury and Holve (1982)
419 to 837	Holve and Kanury (1982)
418	Chan et al. (1985)
1256	Miller and Ramshalli (1986)
500*	Sibulkin (1986)
360	Gandhi and Kanury (1988)
1464 (tars)	Curtis and Miller (1988)
−301 (char, gases)	
0	Atreya and Wichman (1989)
600	Bennini et al. (1991)
20 (low conversions)	Koufopanos et al. (1991)
−255 (high conversions)	

[a] All values on a per unit mass of volatiles basis, unless noted by *, which indicates a unit mass of solids basis.

Appendix J

IRR calculation:

BPAC PLANT
ECONOMIC ANALYSIS

	Total	Year	Year	Year	Year	Year	Year	Year	Year	Year	Year	Year
		0	1	2	3	4	5	6	7	8	9	10
		2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
	$	$	$	$	$	$	$	$	$	$	$	$
Capital expenditure												
Establishing the BPAC Plant	-10,442,538	-10,442,538	0									
	-10,442,538	-10,442,538	0	0	0	0	0	0	0	0	0	0
Profit and loss account												
Revenue	52,272,000	0	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200
Operating costs	16,842,244	0	1,684,224	1,684,224	1,684,224	1,684,224	1,684,224	1,684,224	1,684,224	1,684,224	1,684,224	1,684,224
Cash operating costs	27,284,782	0	2,728,478	2,728,478	2,728,478	2,728,478	2,728,478	2,728,478	2,728,478	2,728,478	2,728,478	2,728,478
Depreciation	-10,442,538	0	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254
Profit before taxation	35,429,756	0	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976
Income tax	-3,616,920	0	0	293,593	293,593	293,593	-749,617	-749,617	-749,617	-749,617	-749,617	-749,617
Profit after taxation	31,812,836	0	3,542,976	3,836,569	3,836,569	3,836,569	2,793,359	2,793,359	2,793,359	2,793,359	2,793,359	2,793,359
Income tax calculation												
Profit before taxation per above	35,429,756	0	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976	3,542,976
Add : back depreciation	-10,442,538	0	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254	-1,044,254
Less : Capital allowances	-10,432,096	0	-3,477,365	-3,477,365	-3,477,365	0	0	0	0	0	0	0
Taxable profit/(loss)	14,555,122	0	-978,643	-978,643	-978,643	2,498,722	2,498,722	2,498,722	2,498,722	2,498,722	2,498,722	2,498,722
Tax rate			30.00%	30.00%	30.00%	30.00%	30.00%	30.00%	30.00%	30.00%	30.00%	30.00%
Tax (payable)/saving in following year	-3,616,920	0	0	293,593	293,593	293,593	-749,617	-749,617	-749,617	-749,617	-749,617	-749,617
Cash flow calculations												
Capital expenditure	-10,442,538	-10,442,538	0	0	0	0	0	0	0	0	0	0
Revenue	52,272,000	0	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200	5,227,200
Cash operating costs	-27,284,782	0	-2,728,478	-2,728,478	-2,728,478	-2,728,478	-2,728,478	-2,728,478	-2,728,478	-2,728,478	-2,728,478	-2,728,478
Tax payments	-3,616,920	0	0	293,593	293,593	293,593	-749,617	-749,617	-749,617	-749,617	-749,617	-749,617
Net cash flow	10,927,760	-10,442,538	2,498,722	2,792,315	2,792,315	2,792,315	1,749,105	1,749,105	1,749,105	1,749,105	1,749,105	1,749,105
Payback			2,498,722	5,291,037	8,083,351	10,875,666	12,624,772	14,373,877	16,122,982	17,872,087	19,621,193	21,370,298

Internal rate of return		17.93%
Return on Investment		23.93%
Payback period (years)		3.8

Tax rate		30.0%
Tax Credits	1st year	33.3%
	2nd year	33.3%
	3rd year	33.3%
Depreciation-straight line		10.0%

Appendix K

Laboratory Pilot Plant