

Co-pyrolysis of Coal and Agricultural Waste

Akinwale Aboyade ¹⁺, Adelaja Osibote ², Ademola Rabiou², Marion Carrier² and Johann Görgens³

¹ Environmental & Process Systems Engineering Research Group, Chemical Engineering Department, University of Cape Town, Rondebosch 7701, South Africa

² Energy and Nuclear Sciences Research Group, Faculty of Applied Sciences, Cape Peninsula University of Technology, Cape Town 8000, South Africa

³ Process Engineering Departments, Stellenbosch University, Stellenbosch 7602, South Africa

Abstract. Co-utilizing of coal and agricultural plant waste in existing coal based gasification/synthesis installations is widely recognized as a potentially realistic starting scenario for the production of second generation biofuels. Updraft, fixed-bed gasifiers are currently the most commercially successful gasifiers used for coal gasification and are known produce significant quantities of pyrolysis derived tar along with syngas. In order to investigate the pyrolysis of coal-biomass blends, a pressurized fixed-bed pyrolyzer was employed with coal-biomass blends of 100:0 95:5, 50:50, and 0:100 wt%. Sugarcane bagasse was selected as the biomass feedstock because of its relative prevalence in South Africa. In this study, the effect of adding biomass to coal on the distribution of pyrolysis products were evaluated with attention focused on volatile product yields and composition. It was determined that synergistic or non-additive interactions between biomass and coal impacted on the ability to predict the yields of specific liquid condensate products.

Keywords: Sugarcane bagasse, Coal, Co-pyrolysis, Co-gasification, Updraft, Fixed bed, Condensate, Volatiles

1. Introduction

Concerns in the last few decades regarding the environmental and socio-economic impacts of the dependence on fossil fuels have resulted in calls for more renewable and alternative energy sources. This has led to recent interest in the co-utilization of coal with biomass in industrial coal-based thermochemical conversion processes such as combustion, liquefaction and gasification. Co-processing biomass with coal will not just reduce fossil-derived CO₂ emissions, but can also limit the discharge of local air pollutants such as SO_x and NO_x [1,2]. Co-processing biomass with coal provides further advantages; it helps to avoid costs related to setting up dedicated biomass based installations, and also reduces concerns regarding supply security of biomass feedstock at the levels that will sustain industrial scale processes [1].

Updraft, fixed bed dry bottom gasifiers are the most commercially successful gasifiers in use partly because they generally are of relatively simple construction and operation compared to other common gasifier types, and also because of their high carbon conversion and lower ash carryovers in the product gas stream. Tars are produced in the pyrolysis/devolatilization zone situated in the upper section of updraft gasifiers where a significant proportion mixes with the exiting product gas. In some coal gasification applications, the tar is processed separately from syngas into valuable by-products using techniques similar to those used in oil refineries on conventional fuels.

This paper investigates the effects of possible synergistic interactions between coal and biomass on the yield and composition of volatile products during pressurized co-pyrolysis. The coal samples used was a mix

⁺ Akinwale Aboyade. Tel.: + 27 (0)76 747 7331
E-mail address: wale.aboyade@gmail.com

of typical inertinite rich South African coals, while biomass used was sugarcane bagasse, which along with corn residue make up the bulk of agricultural wastes in South Africa [3]

2. Methodology

The coal sample used was a blend of various typical South African hard coals that can be described as low grade, high ash and inertinite rich coal. Sugarcane bagasse (BG) was obtained from farms in the Kwazulu Natal province of South Africa. BG was received relatively untreated with 35-40% moisture content and then air dried for 48 hours to a moisture content of approximately 10% before being milled to <2mm. Representative sub-samples for experiments were obtained for all samples according to CEN/TS 14780/2005.

Pyrolysis products were obtained using the packed bed reactor set-up [4]. The equipment is able to produce gas, condensates and char under pressurized slow pyrolysis conditions. The apparatus consists of a steel autoclave heated slowly at between 10-15°C min⁻¹ by surrounding heating elements. The pressure is controlled by the back pressure valve. Samples are loaded in the 2L autoclave and sealed with the help of gaskets and steel bolts. The inert carrier gas – nitrogen – flows through the reactor from the bottom at 2.1 L min⁻¹. Gas flow continues for the duration of the experiment and afterwards while the reactor is allowed to cool until no further volatile effluence is observed (usually 2-4 hours).

Two separate condensate traps were employed to trap liquids. The first cold trap collected tars and water at 0-2.5°C in an ice bath. Lighter condensables in the form of aerosols that escaped this trap were then collected using a methanol solvent trap placed in an acetone and ice bath at a temperature of -15°C. The ensuing gas is directed to a gas bag for collection, but samples are also taken at selected temperature ranges during the duration of the tests by using a bypass valve. The heavy molecular weight condensates trapped in the first ice bath consisted of an aqueous and oily (water-insoluble) phase. The phases were separated using Dean and Stark's distillation method (ASTM D244) with toluene as solvent. The tar, aqueous phase, and condensed aerosols were analysed by GC-MS

3. Results

3.1. Yields of lumped products

Yields of the major product classes obtained from pyrolysis of the individual fuels are presented in Fig. 1 as baseline for investigating the influence of mixing during co-pyrolysis. Fig. 1a shows the distribution of the products lumped into solid, liquid and gas phase obtained from high pressure pyrolysis of individual fuel samples. Higher volatile yields (i.e. gas and liquid) and correspondingly lower char yields were obtained from biomass compared to similar results from coal, in line with reported proximate characteristics for these materials [5].

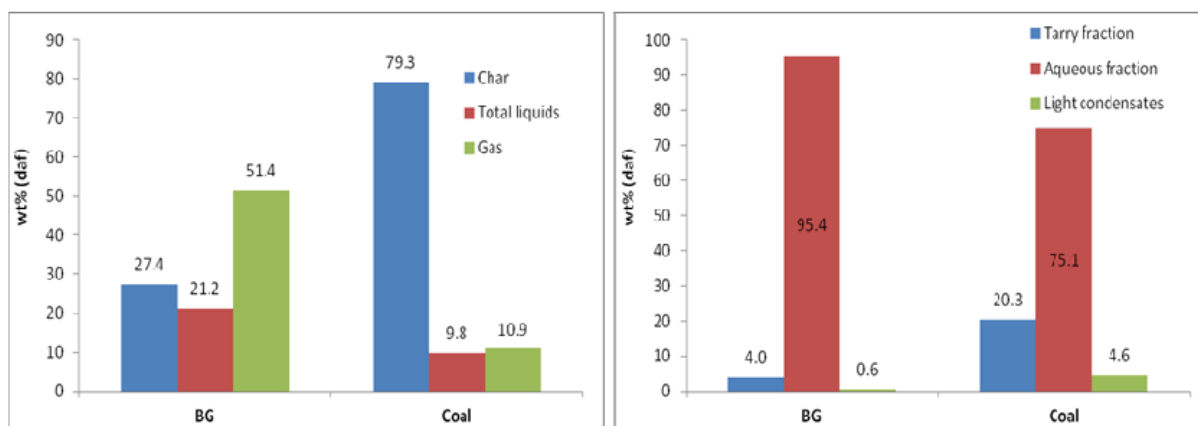


Fig. 1: Pyrolysis yields of a) major product classes and b) distribution of liquid phase products from slow pyrolysis of BG and Coal at 600°C, and 26 bars[4]

Fig. 1b shows the relative distribution of the various liquid fractions that make up total liquids. The aqueous product fractions were split to show the contribution of initial water content and pyrolytic (or ‘bound’) water. Pyrolysis liquids from all fuels are dominated by the aqueous fraction which represents about 95 and 73 wt% of total liquid product for BG and coal respectively. The ratio of gas to liquid yields was 2.4 for BG compared with 1.1 for coal.

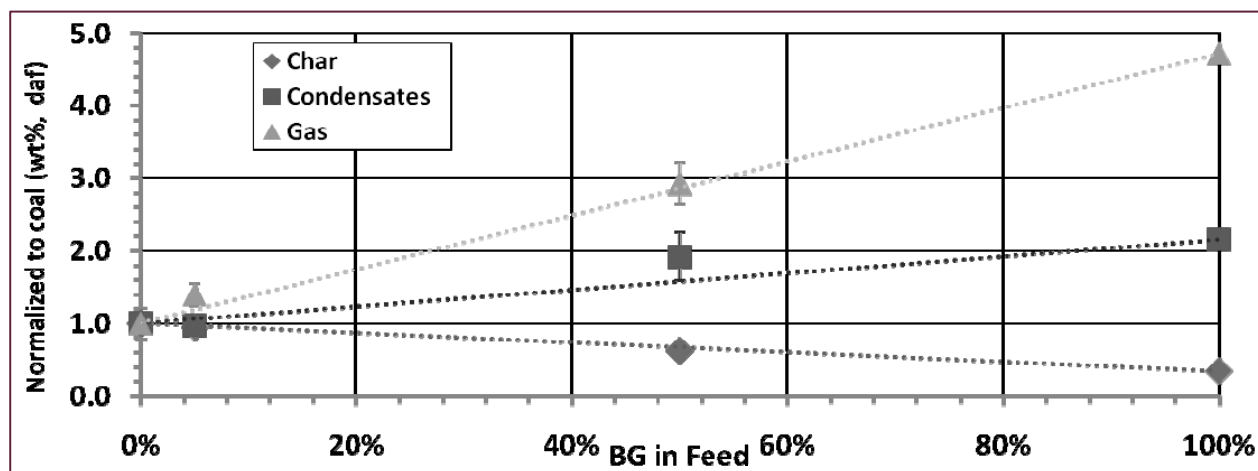


Fig. 2: Influence of mix ratio on distribution of major product classes (values shown are average of three runs and the error bars represent the standard deviation between runs) [4]

Fig. 2 compares the lumped product yields obtained from experiments on the individual pyrolysis of coal and BG with those from coal-BG blends at 50:50 and 95:5 mix ratios. Gas yields were observed to increase by 68% and 350% when 5% and 50% respectively of BG was added. The results also show that measured gas and condensate yields were slightly higher than predicted for the blends, and the disparity was higher for 50:50 than 95:5 mix ratios. However, deviation between measured and predicted values of overall product yield were generally within experimental error as depicted by error bars in the plots. The proportionality between product yields and wt% biomass shown in these results were consistent with results from previous reports [6]

3.2. Condensate composition

The chemical components in the combined condensate fractions obtained from the blends were identified and quantified by GC-MS. 44 hydrocarbon compounds were detected in total from the various fractions of condensates obtained from coal, whereas 63 were detected for BG. These compounds were grouped into the following functional groups; acids, alcohols, aldehydes, esters, furans, ketones, nitriles, single ring aromatics, PAHs, and phenolics. The results show the influence of coal-biomass blend ratios on the yields of the chemical groups. Significant and highly irregular deviations between predicted and observed values can be observed showing that there is no direct proportionality between coal-biomass mix ratios and the yields of the various chemical groups. The same trend could be observed when the individual species which make up the chemical groups are compared (data not shown). One of the main research issues in the study of co-pyrolysis is question of synergy, and whether it can be expected under industrial conditions during co-processing of biomass and coal. The present study demonstrated that the lumped yields of chars, aqueous liquids, tar and gas products obtained from co-pyrolysis of coal with biomass, matched well with values calculated based in the absence of synergistic or additive effects, within experimental error. Many previous reports [6,7] based on experiments conducted under mostly under atmospheric conditions show the same non-additive trend for volatile and char yields during co-pyrolysis.

In contrast to lumped product yields, a distinct non-proportionality was observed between coal-biomass mix ratios and the observed yields of specific volatile species and functional groups such as H₂, CO, CO₂, CH₄, acids, furans, ketones, phenolics, PAHs and other mono and heterocyclic aromatics (Table 1).

Table 1: Influence of mix ratio on composition of chemical groups as a percentage of total liquid hydrocarbons produced (% diff refers to percentage difference between experimental and predicted values)

wt% of liquid HCs	BG fraction in blend					
	0%	5%		50%		100%
		Experimental	% diff	Experimental	% diff	
Acids	0.61	14.36	441.18	19.07	-9.54	41.55
Alcohols	0.95	1.48	22.90	2.61	-24.81	5.99
Aldehydes	0.00	0.03	62.71	0.02	-86.47	0.27
Aromatics	5.12	13.13	163.29	11.42	199.21	2.52
Furans	0.63	5.67	752.94	4.19	340.38	1.27
Heterocyclics	0.24	0.32	37.91	0.30	66.17	0.13
Ketones	8.82	9.17	5.39	13.28	75.00	6.35
Nitriles	0.03	0.17	386.42	0.14	75.82	0.12
PAHs	35.58	6.64	-80.76	4.04	-83.86	14.48
Phenolics	48.02	48.53	3.37	44.20	18.55	26.56
Total oxygenates	50.21	70.06	35.98	70.09	10.72	76.39
PAH's+aromatics	40.93	20.10	-49.43	15.77	-45.68	17.13

This suggests the presence of significant chemical interactions in the vapour phase between volatiles obtained from the contributing feedstocks some of which were described in the previous section. For instance, the increase in acids was significantly beyond what would be expected assuming no interactions. There was also a comparably less drastic increase in the composition of total oxygenates at the various mix ratios, and a corresponding decrease in the percentage of mono and polycyclic aromatics (Table 2). This trend is in agreement with previous observations by Jones et al., [8] in their study of the atmospheric, slow heating rate co-pyrolysis of coal and pinewood. A number of reaction pathways have been suggested for the production of PAHs including the decomposition of long chain aromatics within the coal structure [9] and via the Diels-Alder reaction which involves aromatization and dehydrogenation of aliphatics liberated during coal devolatilization [10]. PAHs can also be produced via the deoxygenation of phenols and cresols or via recombination of phenyl and other aromatic radicals [11]. Phenols are derived from the catechol isomers (o,m,p dihydroxybenzene) within the coal [12]. Catechols are also found in lignin which is responsible for the phenol and cresol derivatives produced from lignocellulosic biomass [13].

4. Acknowledgements

This research was supported by the South African Department of Science and Technology (DST) and the National Research Foundation (NRF), through their Technology and Human Resources for Industry Programme (THRIP). There were also contributions from Sasol Technology, the Fort Hare Institute of Technology, and Cape Peninsula University of Technology (South Africa). The authors gratefully acknowledge their support in publishing this work. The opinions expressed in this paper are those of the authors and are not necessarily to be attributed to the sponsors.

5. References

- [1] R. Davidson, A. Doig, J. Ekmann, R. Fernando, N. Harding, R. Moreea-Taha, et al., Cofiring coal with other fuels, IEA Clean Coal Centre, 2007.
- [2] N. Koukouzas, A. Katsiadakis, E. Karlopoulos, E. Kakaras, Co-gasification of solid waste and lignite—A case study for Western Macedonia, Waste Management. 28 (2008) 1263–1275.
- [3] L.R. Lynd, H. Von Blottnitz, B. Tait, J. de Boer, I.S. Pretorius, K. Rumbold, et al., Converting plant biomass to fuels and commodity chemicals in South Africa □: a third chapter?, South African Journal of Science. 99 (2003) 499–507.
- [4] A.O. Aboyade, Co-gasification of coal and biomass: Impacts on syngas and condensate production,

Stellenbosch University, 2012.

- [5] A.O. Aboyade, M. Carrier, E.L. Meyer, J. Gorgens, J.H. Knoetze, Model fitting kinetic analysis and characterisation of the devolatilization of coal blends with corn and sugarcane residues, *Thermochimica Acta*. 530 (2012) 95–106.
- [6] B. Moghtaderi, C. Meesri, T.F. Wall, Pyrolytic characteristics of blended coal and woody biomass, *Fuel*. 83 (2004) 745–750.
- [7] A.G. Collot, Y. Zhuo, D.R. Dugwell, R. Kandiyoti, Co-pyrolysis and co-gasification of coal and biomass in bench-scale fixed-bed and fluidised bed reactors, *Fuel*. 78 (1999) 667–679.
- [8] J.M. Jones, M. Kubacki, K. Kubica, A.B. Ross, A. Williams, Devolatilisation characteristics of coal and biomass blends, *Journal of Analytical and Applied Pyrolysis*. 74 (2005) 502–511.
- [9] K.H. Van Heek, W. Hodek, Structure and pyrolysis behaviour of different coals and relevant model substances, *Fuel*. 73 (1994) 886–896.
- [10] K. Unapumnuk, A Study of the Pyrolysis of Tire Derived Fuels and an Analysis of Derived Chars and Oils, PhD Thesis, University of Cincinnati, 2006.
- [11] R.J. Evans, T.A. Milne, Molecular characterization of the pyrolysis of biomass, *Energy and Fuels*. 1 (1987) 123–137.
- [12] M.J. Wornat, E.B. Ledesma, N.D. Marsh, Polycyclic aromatic hydrocarbons from the pyrolysis of catechol (ortho-dihydroxybenzene), a model fuel representative of entities in tobacco, coal, and lignin, *Fuel*. 80 (2001) 1711–1726.
- [13] T. Hosoya, H. Kawamoto, S. Saka, Pyrolysis behaviors of wood and its constituent polymers at gasification temperature, *Journal of Analytical and Applied Pyrolysis*. 78 (2007) 328–336.