In-Situ Catalytic Upgrading of Bio-oil using Mo_2C/Al_2O_3

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Objectives

In situ bio-oil upgrading via catalytic pyrolysis of ground sugar cane bagasse pellets (SCBP) with use of molybdenum carbide (20% Mo_2C/Al_2O_3) catalyst.

Introduction

Currently, sugarcane bagasse is recovered for use as a fuel in deliberately inefficient burners to produce electricity for sugar mills. Alternative, more efficient processes could be used to maximise the energy output from bagasse. Thermally processing SCBP increases throughput and improves feeding compared to sugarcane bagasse (Figure 1). Fast pyrolysis bio-oil is acidic and has a high solid, water and oxygen content. However, catalytic pyrolysis can be used to improve bio-oil properties.

Figure 1. Sugarcane bagasse (left) Sugarcane bagasse pellets (right)

Experimental and Characterisation

Al_2O_3 (CATAPAL A – PP1688) was used as a support for β-Mo_2C. MoO_3/Al_2O_3 samples were prepared prior to β-Mo_2C/Al_2O_3 synthesis with a nominal content of 20 wt.% MoO_3 using the incipient wetness impregnation method. After the impregnation of the solution the material was left to dry completely in a furnace kept at 393 K overnight. After this step, the sample was calcined at 773 K for 3h. The 20 wt.% MoO_3/Al_2O_3 sample was carburized using the temperature-programmed carburization (TPC) methodology to obtain molybdenum carbide (β-Mo_2C/Al_2O_3).

TGA pyrolysis of SCBP helped determine the volatile and char content. Table 1 summarises the proximate and elemental analysis.

Table 1. Proximate and elemental analysis of SCBP

C	46.56wt.%
H	5.74wt.%
N	0.3wt.%
O	47.37wt.%
S	Nm
Ash	5.71wt.%
HHV (MJ/kg)	18.11
Volatiles	75.85wt.%
Char	24.15wt.%

Ground SCBP were screw fed into a 300 g/h continuous fast pyrolysis reactor (Figure 2) operated at 500 °C. Different concentrations (0 wt.%, 12 wt.%, 25 wt.% and 50 wt.%) of Mo_2C/Al_2O_3 replaced the sand in the fluidised bed reactor. Bio-oil chemical composition was analysed using GC-MS.

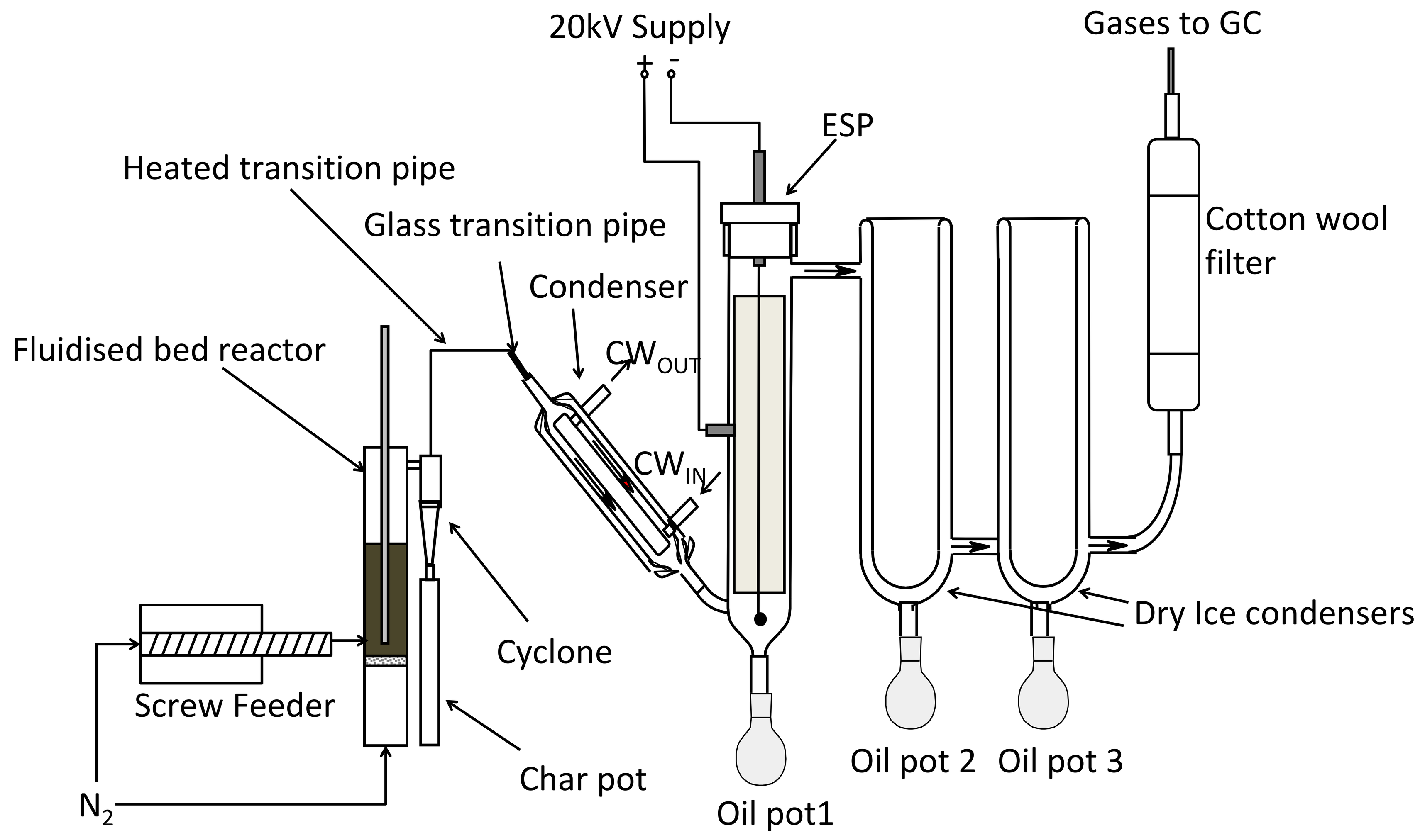

Figure 2. Continuous fluidised bed fast pyrolysis system

Results and Discussion

Fast pyrolysis of SCBP yields 73.14 wt.% total liquid (60.45 wt.% organic liquid) on dry feed basis. Table 2 shows that increasing the concentration of Mo_2C/Al_2O_3 from 0 wt.% to 50 wt.% reduced organics and increased water yield.

Table 2. Mass balances of catalytic pyrolysis of SCBP

Wt% of Mo_2C/Al_2O_3 catalyst	0 wt. %	12 wt.%	25 wt.%	50 wt.%
Char (wt.%)	17.32	16.49	28.82	27.13
Total liquid (wt.%)	73.14	66.41	60.70	61.71
Organic liquid (wt.%)	**60.45**	**49.45**	**43.33**	**39.30**
Total water content (wt.%)	**12.69**	**16.96**	**17.37**	**22.41**
Gas (wt.%)	14.01	20.14	19.63	14.47
Recovery (wt.%)	93.83	92.41	98.53	92.69

Figure 3 shows that the use of molybdenum carbide leads to a reduction in the levoglucosan yield, which was accompanied by an increase of furans and phenols yields.

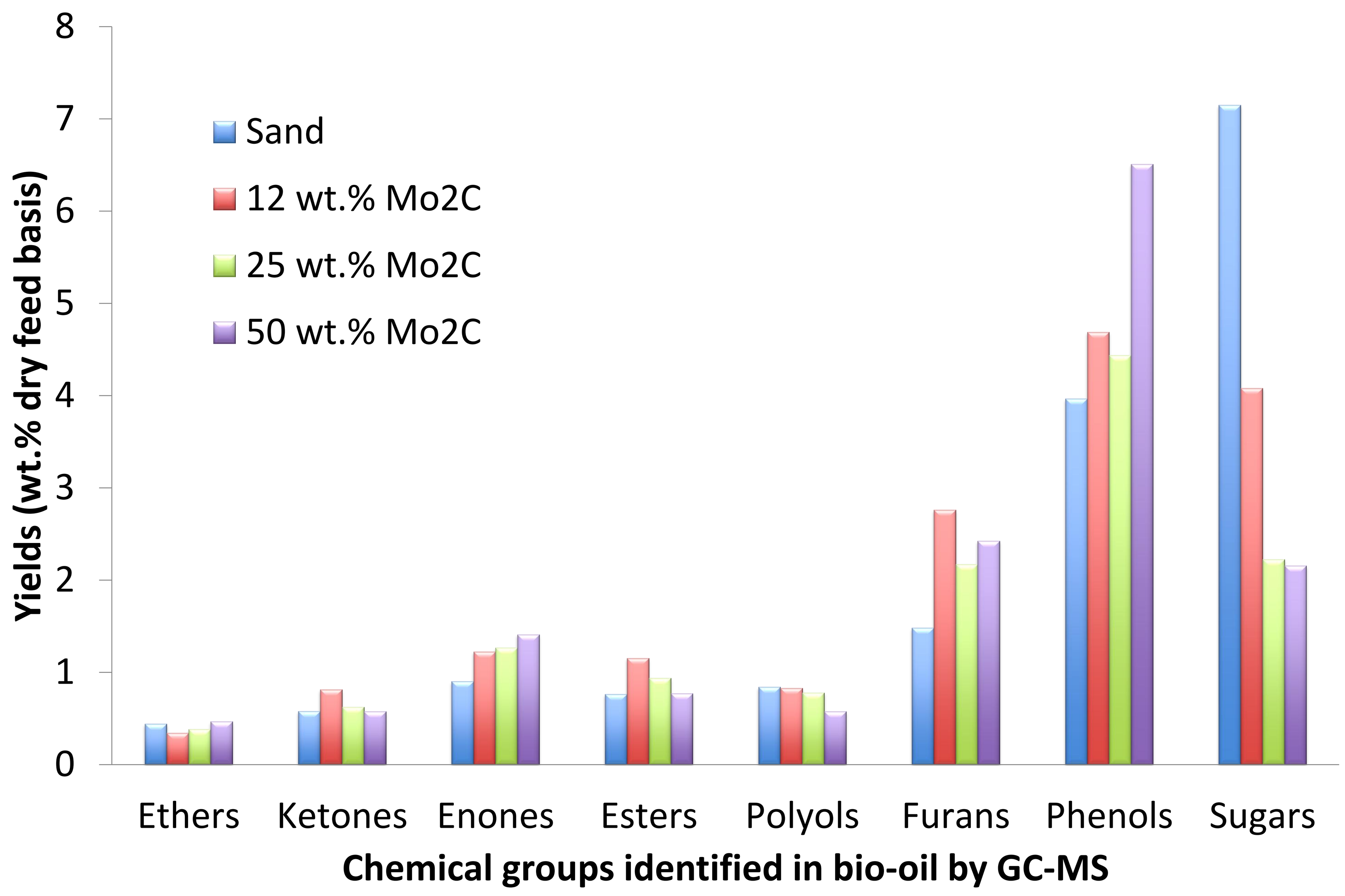

Figure 3. Effect of Mo_2C/Al_2O_3 concentration on bio-oil composition

Polydispersity (PDI) results indicate an improved molecular homogeneity when introducing Mo_2C/Al_2O_3 up to 12 wt.%. Bio-oil viscosity and flow properties are improved with increasing catalyst concentration as a result of increased water content.

Table 3. Viscosity and PDI with increasing catalyst concentration

Catalyst concentration	Viscosity (cP) @ 40 °c	Polydispersity Index (PDI)
Sand (0wt. % Mo_2C/Al_2O_3)	2780	1.66
12 wt. % Mo_2C/Al_2O_3	71.5	1.41
25 wt.% Mo_2C/Al_2O_3	19.7	1.41
50 wt.% Mo_2C/Al_2O_3	8.2	1.41

Conclusions

- **Mo_2C/Al_2O_3 can be added to the fluidised bed reactor without becoming coked.**
- **Addition of Mo_2C/Al_2O_3 improves the viscosity and homogeneity of bio-oil. These improved bio-oil properties are crucial if liquid bio-oil is to be further upgraded.**
- **Mo_2C/Al_2O_3 increases furan and phenol content in bio-oil. Furans are valuable starting products for speciality materials. Phenols can be used for the production of phenolic resins and other petrochemical products.**
- **While furans are reported to be derived catalytically from sugars such as levoglucosan, phenols derive from lignin.**
- **Mo_2C/Al_2O_3 reduces bio-oil sugars content. Sugars and acids are responsible for the acidity of bio-oil.**

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SEVENTH FRAMEWORK PROGRAMME

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