

# Effect of CaO on tar production and dew point depression during gasification of fuel cane bagasse in a novel downdraft gasifier

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## ARTICLE INFO

### Article history:

Received 4 June 2012

Received in revised form 15 September 2012

Accepted 28 September 2012

Available online 7 November 2012

### Keywords:

Biomass  
Catalytic gasification  
Downdraft gasifier  
Gasification  
Syngas  
Tar

## ABSTRACT

Granular calcium oxide was used in syngas conditioning to investigate its impact on tar composition, concentration, dew point and syngas yield during gasification of fuel cane bagasse (FCB). The results showed that the use of 2, 3 and 6 wt.% in-bed CaO promoted the conversion of Class 1, 4 and 5 tars to Class 3 tars to varying degrees. Overall, this resulted in a decrease in tar yield ranging from 16 to 35%, a decrease in the tar concentration in syngas of 44–80%, an increase in syngas yield of 17–37%, and a decrease in tar dew point of 37–60 °C as the CaO concentration was increased from 2 to 6 wt.%.

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## 1. Introduction

Gasification is the conversion of solid organic material into a syngas rich in H<sub>2</sub> and CO by partial oxidation at temperatures greater than 500 °C [1]. It has emerged as one of the primary energy conversion technologies for sustainable energy production, particularly from low heating value biomass residues, due to the higher efficiencies of conversion of fuel to energy as compared to combustion.

During gasification condensable organic compounds known as tars are produced and become entrained in the syngas [2,3]. Tars can cause widespread fouling of operating equipment as they can condense on downstream users causing extensive coking of heat exchangers and plugging of valves. Consequently in most post gasification applications, including power generation and gas to liquid conversion, tars must be removed to varying degrees using various techniques [2].

Biomass fuels high in lignin such as fuel cane bagasse (FCB), yield higher concentrations of tar compared with other fuels such as bone meal or municipal solid waste which contain catalytic contaminants useful in tar cracking [4–7]. According to van Paasen and Kiel [8] these compounds can be classified into five classes on the basis of their condensation behaviour and water solubility. In this classification system the potential for condensation of a given composition of tars is

determined by calculating the tar dew point which is defined as the temperature at which the real total partial pressure of tar equals the saturation pressure of tar [9]. Since tars can condense and deposit onto surfaces when cooling of syngas occurs, determination of the tar dew point is a major consideration for commercialisation of biomass gasification systems as it facilitates an evaluation of the potential impact on downstream equipment. The classification system outlined by van Paasen and Kiel [8] and the tar dew point for each class are outlined in Table 1.

Evidently, the concentrations of separate tar compounds have limited practical usefulness; instead, the tar dew point is a critical measure of the overall effect of tars on downstream operating systems. It can be seen from Table 1 that at very low concentrations of Class 4 and 5 tars, these compounds will condense even at high temperatures. Conversely, Class 2 and 3 tars condense only at extremely high concentrations and temperatures below 0 °C [8].

Tars not only cause fouling of downstream process equipment but can represent as much as 10% of the low heating value of the syngas produced which is lost to the syngas if not converted to H<sub>2</sub>, CO and CH<sub>4</sub> [9,10]. The production of tar therefore lowers the overall conversion efficiency of biomass to syngas and increases the capital operating costs. Consequently the reduction and/or removal of tar from syngas is critical to the widespread development of commercial small-scale biomass gasifier systems since syngas from air blown gasifiers has relatively low calorific value compared with natural gas.

Currently, the preferred option for tar reduction is in the gasifier itself through process control and the use of primary measures such as additives and catalysts which modify gasification conditions [5–7,10–14].

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**Table 1**  
Classification of tar compounds.

Tar class	Classification	Tar compounds	Tar dew point
Class 1	GC-undetectable	Very heavy polyaromatic compounds, 7 or more rings	Very high tar dew point, actual temperatures and concentrations are not known.
Class 2	Heterocyclic aromatics	Cyclic hydrocarbons with heteroatoms, highly water soluble e.g. phenol, cresol and pyridine	<−50 °C at 10000 mg Nm <sup>−3</sup>
Class 3	Light aromatic	Compounds that usually do not cause problems as a result of condensation or water solubility e.g. toluene, styrene and xylene	<−50 °C at 10000 mg Nm <sup>−3</sup>
Class 4	Light polyaromatic	2 and 3 ring compounds that condense at intermediate temperatures at relatively high concentrations e.g. naphthalene, phenanthrene and anthracene	> 10 °C at ≥ 1 mg Nm <sup>−3</sup>
Class 5	Heavy polyaromatic	4–6 ring compounds that condense at high temperature and low concentrations e.g. fluoranthene, pyrene, chrysene, perylene and benzo(ghi) perylene	≥ 120 °C at 0.1 mg Nm <sup>−3</sup>

One such cheap additive is calcium oxide (CaO), which is widely known to have a catalytic effect on the decomposition of tar species during biomass gasification. Many researchers [15–18] have reported that the use of calcium based oxides derived from limestone and dolomite improved the efficiency of gasification as well as the yield and low heating value of the syngas produced in atmospheric and steam gasification in fluidised bed gasifiers. Several workers using fluidised bed gasifiers have shown that calcined dolomite (Mg–O–CaO) and calcites (CaO) used as in bed catalysts at concentrations ranging from 2 wt.% to 10 wt.% have resulted in tar destruction efficiencies up to 95% [15–18]. To date however there is no published data on the effect of in-bed CaO on tar production during gasification in small-scale fixed bed downdraft gasifiers.

Owing to the distributed nature of biomass, these modular small-scale gasifier systems are ideally suited for distributed generation. They therefore represent a practical solution for sustainable energy production in small economies, rural areas far removed from a central grid and as part of a waste management strategy for companies disposing large volumes of biomass waste. Thermal conversion of biomass to chemicals, biofuels and power through syngas generation by gasification and subsequent syngas cleaning, gas separation and syngas-to-liquid conversion simultaneously with electricity generation by fuel cells or internal combustion engines constitute the major unit operations of a sustainable biorefinery even at low production capacity [19]. Indeed, such distributed and integrated production platforms are already under development at small-scale [20].

This study investigated the effects of in-bed CaO as a primary measure on tar concentration, composition, conversion, dew point and syngas yield during gasification of FCB which is the waste residue from an energy crop known as fuel cane.

## 2. Materials and methods

### 2.1. Fuel cane bagasse

Fuel cane, grown at various locations in Barbados (13° 10N, 59° 32W) and at elevations ranging from 60 to 90 m was harvested by mechanical harvesters in February during the dry season. They were

cut approximately 15 cm above ground and the stalk, cane tops and trash were immediately loaded unto trailers and delivered to the Portvale sugar factory where sugar was extracted within 48 h of harvesting. To avoid changes in biomass structure caused by complete drying, the bagasse produced was then air dried outdoors in covered areas at ambient conditions (32 °C) to a moisture content of 20–25 wt.%. After drying, the bagasse was sealed in polypropylene bags and shipped over a two week period to the United Kingdom for use in this study. On arrival at the laboratory in the UK, the FCB was air dried indoors at laboratory-ambient conditions. During this time the heaps were mixed every two days to ensure even drying and the moisture content monitored periodically until equilibrium with the ambient atmosphere (9.4–10 wt.%, dry basis) was obtained. It was then shredded in a hammer mill and pelletised into 8 mm diameter pellets using a Swedish Power Chippers AB commercial pellet press PP300, the final moisture content of the pellets ranged from 6.0 to 7.4 wt.% (dry basis).

The proximate and ultimate analyses of the FCB are presented in Table 2.

### 2.2. 50 kWe air-blown downdraft gasifier

A schematic of the downdraft gasifier system used in this work is shown in Fig. 1. Gasification of FCB was carried out at atmospheric pressure in an intensified autothermal air-blown 50 kWe throated downdraft gasifier [21] which is illustrated diagrammatically in Fig. 1. The reactor has a double wall and heat loss is further reduced by fibreglass lagging which covers the outer shell. The basic gasification system was described in [4,5,22] and has been scaled up to 2 MWe for commercial applications. The performance of the gasifiers at 50 kWe and 1 MWe levels was compared and found to be very similar [4,5,22].

Briefly, fuel is batch fed manually into the reactor through the hopper at the top; after loading the gasifier the induced draft fan is switched on and the reactor started by manually lighting the air inlet ports with a butane torch. Air, the gasifying agent, is sucked into the gasifier through the main air inlet valve at a controlled flow rate and into the chamber surrounding the throat by the induced draft fan. From there the air then flows into the oxidation zone through a plane of air nozzles. The syngas generated in the gasifier is then extracted from the reactor by the suction effect of the induced draft fan. As the solid fuel is converted to syngas, this causes the remaining fuel to flow down through the reactor under gravity. The

**Table 2**  
Proximate and ultimate analysis of fuel cane bagasse.

Ultimate analysis		
Carbon (wt.%)		49.4 ± 0.03
Hydrogen (wt.%)		6.3 ± 0.3
Oxygen* (wt.%)		43.9 ± 0.5
Nitrogen (wt.%)		0.30 ± 0.06
Sulphur (wt.%)		0.07 ± 0.01
Chlorine (wt.%)		0.05 ± 0.01
High heating value (HHV) MJ kg <sup>−1</sup>		18.9 ± 0.3
Low heating value (LHV) MJ kg <sup>−1</sup>		17.6 ± 0.2
Proximate analysis		
Moisture (wt.%)		9.4 ± 0.8
Volatile matter (wt.%db)		65 ± 5
Fixed carbon (wt.%db)		31 ± 4
Ash (wt.%db)		3.6 ± 0.7
Size and bulk density		
Bagasse type	Size (mm)	Density (kg m <sup>−3</sup> )
Fibrous bagasse	0.09–4.0	68 ± 5
Pelletised bagasse	D = 8 mm	727 ± 3

db – dry basis.

\* Calculated by difference.

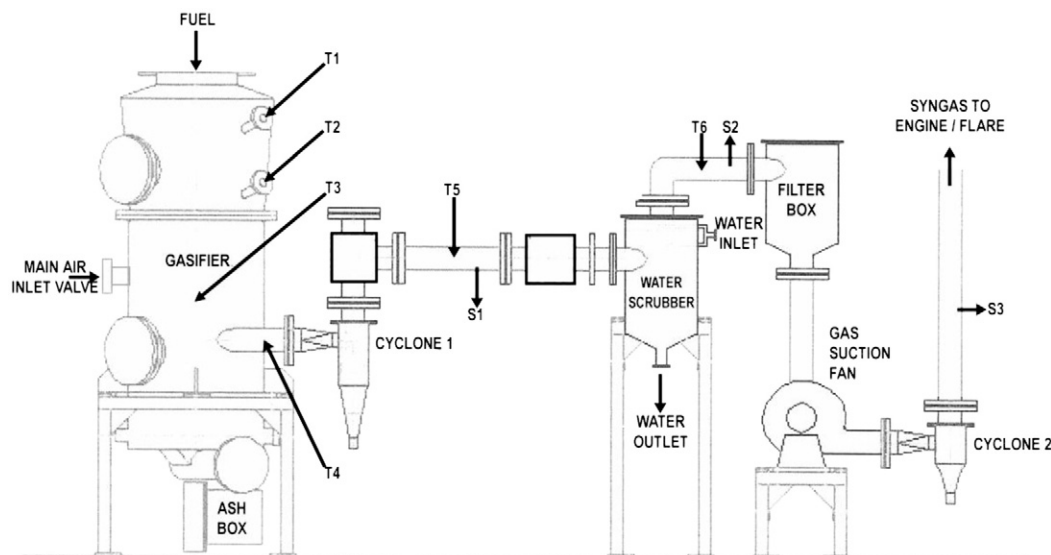


Fig. 1. Newcastle University 50 kW gasifier system.

ash and char produced during gasification were manually emptied into the ash box by turning the ash box handle periodically during gasification. Thermocouples located at T1 (drying zone), T2 (pyrolysis zone), T3 (oxidation zone) and T4 (reduction zone) continuously monitor the gasification zone temperatures. Each of the thermocouples hangs in the centre of the vessel so as to minimise any influence on temperature caused by wall effects. Online syngas sampling and analysis were carried out by the Agilent HP 6890 gas chromatograph (GC) connected at sampling point S3 whilst syngas samples were collected manually in gas tight Tedlar sample bags at sampling points S2 and S3. These samples were also analysed by GC.

### 2.3. Experimental conditions

#### 2.3.1. Gasification of fuel cane bagasse

Gasification was carried out under optimal operating conditions for FCB [21]. Prior to investigating the effect of in-bed CaO, 6 experimental runs were carried out. In these runs approximately 150 kg of pelletised bagasse was gasified, the equivalence ratio (ER) was 0.26 and the gasification of pelletised FCB could be sustained without bridging thus yielding consistent syngas quality. FCB with a moisture content of 11.5 wt.% was used in these experiments; the typical operating temperatures in the pyrolysis zone were  $716 \pm 66$  °C and in the oxidation zone  $1040 \pm 130$  °C. The typical molar percentage syngas composition (dry basis) was:  $H_2 = 12.1$ ;  $CO = 17.2$ ;  $CH_4 = 3.6$ ;  $CO_2 = 15.9$ ;  $O_2 = 1.0$  with  $N_2$  representing the balance and trace amounts of  $C_2H_4$  and  $C_2H_6$ . The low heating value (LHV) was  $5.7 \pm 0.6$  MJ/m<sup>3</sup><sub>n</sub> (dry basis) with cold gas efficiency of 82%.

### 2.4. Experimental procedure

#### 2.4.1. In-bed calcium oxide

The impact of CaO on gasification of FCB was investigated in six experimental runs. In a 250 L container, granular CaO and bagasse pellets were mixed manually at 2 wt.%, 3 wt.% and 6 wt.% respectively. The mixed materials were carefully loaded into the gasifier to avoid segregation of the CaO and pellets. No additional runs were carried out with a higher percentage content of CaO due to the unavailability of pellets. The physicochemical properties of the granular CaO used in this study are percentage purity > 90%, bulk density 80–1200 kg m<sup>-3</sup>, particle size 1.0–5.0 mm, pore volume 0.049 cm<sup>3</sup> g<sup>-1</sup> and surface area 5.41 m<sup>2</sup> g<sup>-1</sup>. The effect of in-bed CaO on tar concentration, composition,

dew point and syngas yield was determined by comparison of these parameters with and without CaO.

#### 2.4.2. Tar collection and storage

Tar sampling was carried out according to the draft Tar Protocol CEN/TS 15439:2006 [23] with some modification. Samples of syngas were extracted at gas tight sample ports under isothermal conditions and at a constant flow rate for a minimum period of 1 h from the syngas stream at sampling points S2 and S3 (Fig. 1). To prevent condensation and/or thermal decomposition of target analytes in the sample line, the line was trace heated to 300 °C for the duration of sample collection. The syngas was then bubbled through a heated glass fibre thimble filter at a flow rate of 0.6 Nm<sup>3</sup> h<sup>-1</sup> into a series of three impingers heated to 40 °C and another three contained in a salt and ice bath at –12 °C (standard conditions are defined here according to NIST as 293.15 K and 101.325 kPa) (Fig. 2). All the impingers contained isopropanol (99.9%) and after flow through the impingers the syngas stream was discharged to the atmosphere.

On completion of sample collection, the isopropanol in the impingers was mixed, the impingers and tubing were rinsed with additional isopropanol and the rinsate added to the impinger solutions and stored in an air tight brown bottle at 4 °C until the sample could be analysed.

The tars contained in the glass fibre thimble filters were extracted by Soxhlet extraction over a period of 5 h using isopropanol. After each extraction, 100 ml of the extract was removed and the remainder added to the stored solution collected from the impingers. After Soxhlet extraction the glass fibre filter thimbles were dried in an oven at 105 °C overnight and then cooled in a dessicator. The difference in mass between the initial filter used and the extracted filter represent the mass of particulate matter contained in the sampled syngas. To determine the mass of gravimetric tar contained in the filters, the 100 ml extract was evaporated at 55 °C and 180 mbar using a rotary evaporator and the mass of the residue was recorded. Determination of the GC-detectable tar content of the gravimetric tar was carried out by re-dissolving the residue in 25 ml of isopropanol which was then stored in a sealed brown bottle at 4 °C until it could be analysed by GC/MS as outlined below.

#### 2.4.3. Tar analysis

The sample extracts collected were analysed for tars by gas chromatography/mass spectroscopy (GC/MS) using an HP 5971A GC/MS. The column used was an HP 5MS 30 m × 0.25 mm i.d., 0.25 µm film



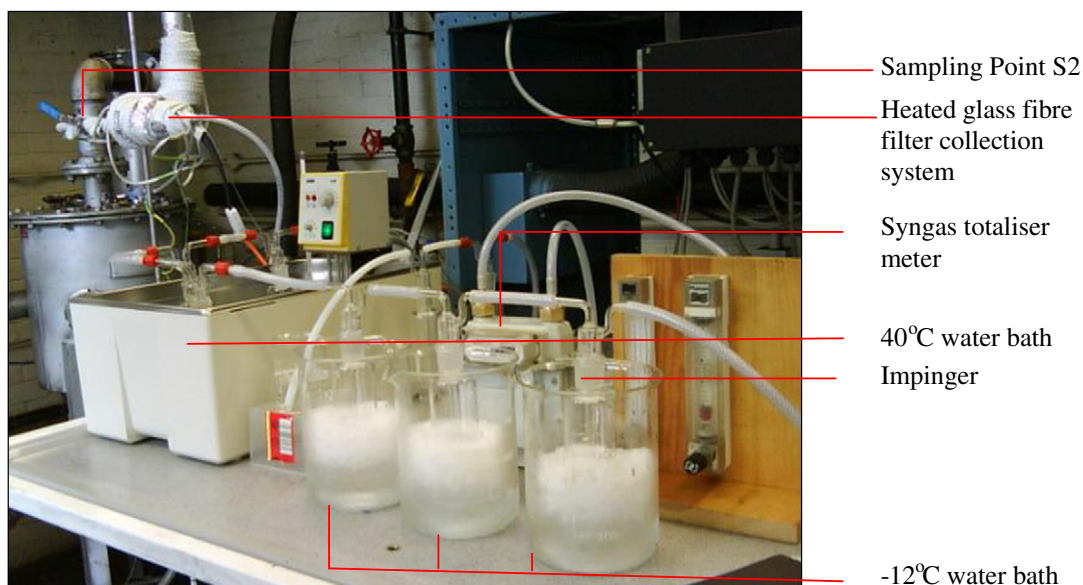


Fig. 2. Tar collection system.

thickness. The carrier gas was high purity helium (99.999%) at a flow rate of  $1.0 \text{ ml min}^{-1}$ . The temperature programme was: initial  $50^\circ\text{C}$  where it was held for 5 min, then to  $325^\circ\text{C}$  at a rate of  $8^\circ\text{C min}^{-1}$ , where it was held for another 5 min. The injector temperature was set at  $250^\circ\text{C}$  and  $2 \mu\text{l}$  of each sample was injected in the split mode with a split ratio of 50:1. The MS was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The transfer line and ion source temperatures were  $280^\circ\text{C}$  and  $160^\circ\text{C}$  respectively. Identification of the tars was done using the NIST spectral library and the MassBank high resolution mass spectral database; quantitative analysis was carried out in full scan mode in the range 50–500 U using internal and external standards.

#### 2.4.4. Tar dew point calculation

The tar dew point of each mixture of tars produced was calculated using the tar dew point model developed by the Energy Research Centre of the Netherlands (ECN) [9]. This model has an accuracy of  $\pm 3^\circ\text{C}$  in the temperature range  $20\text{--}170^\circ\text{C}$  and is the sum of all the dew point values of each tar species present. It is based on the behaviour of ideal gases and Raoult's law and the Antoine equation are applied for calculation of the dew point of a mixture of hydrocarbons, using the vapour pressure data of individual compounds. Only tars with molecular weights between toluene and coronene are considered, the heavier Class 1 tars are not included in the calculation. Since Class 1 tars have high tar dew points at low concentration this means that the actual tar dew point for syngas containing these tars is higher than the calculated value.

### 3. Results and discussion

#### 3.1. Impact of CaO on syngas yield, tar yield and low heating value

With the use of in-bed CaO, an increase in syngas yield ranging from 17 to 37% and a reduction in the tar yield ranging from 16 to 35% were observed as the CaO concentration increased from 2 wt.% to 6 wt.%. Tar yield was determined as a percentage of the initial weight of biomass, on a dry basis. Comparison of the syngas yield and tar yield with and without CaO is illustrated in Fig. 3 and the overall effect of the use of the additive in the reduction of tar and in

increasing gasification efficiency and syngas yield is presented in Table 3.

A 17% increase in syngas yield was observed with the addition of 2 wt.% CaO. When 3 wt.% in-bed CaO was used the syngas yield increased to 23%. However, when the quantity of in-bed CaO was doubled from 3 wt.% to 6 wt.% a 37% increase in syngas yield was observed.

A 16% reduction in tar was found with the use of 2 wt.% CaO and 20% reduction occurred with the addition of 3 wt.% CaO. By doubling the in-bed CaO to 6 wt.% a 35% reduction in tar yield was obtained. The highest cold gas efficiency of 92% was also obtained when 6 wt.% CaO was added to the biomass, and it is evident therefore that of the three concentrations of in-bed CaO evaluated the addition of 6 wt.% CaO resulted in the greatest overall improvement in the reforming of tars and in the conversion of biomass to energy. The percentage increase in  $\text{H}_2$ , CO and  $\text{CH}_4$  with increasing concentration of CaO is outlined in Table 4. From the increase in the production of these gases, it is evident that tar cracking reactions were catalysed by the CaO.

It is widely acknowledged that CaO accelerates the rupture of ringed structures. According to [24–26], the  $\text{O}^{2-}$  ions which form

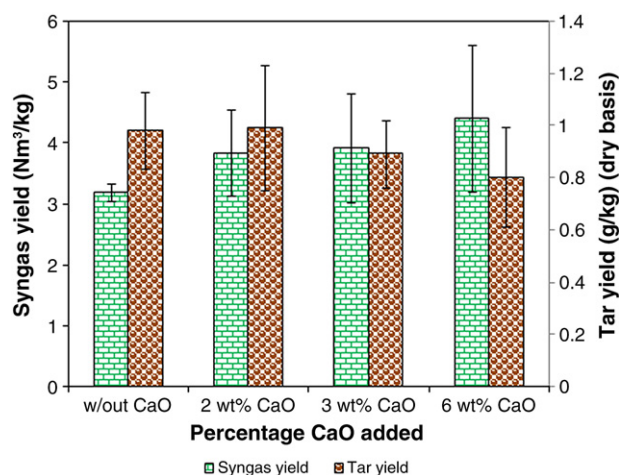


Fig. 3. Change in syngas yield and tar content with the use of in-bed CaO.

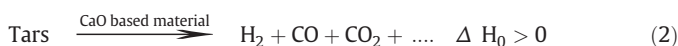
**Table 3**  
Change in low heating value and cold gas efficiency with addition of in-bed CaO.

Parameter	Without CaO	2 wt.% CaO	3 wt.% CaO	6 wt.% CaO
Total tar concentration* (mg Nm <sup>-3</sup> )	621 ± 11	349 ± 54	281 ± 40	123 ± 35
Low heating value (MJ kg <sup>-1</sup> ) (dry basis)	5.7 ± 0.6	5.9 ± 0.1	6.0 ± 0.1	6.2 ± 0.2
Cold gas efficiency (%)	77 ± 9	86 ± 8	91 ± 11	92 ± 13

\* Total tar is defined as the sum of GC-detectable and gravimetric tar.

the active sites on CaO have spatially diffuse electron clouds which disrupt the stability of the  $\pi$ -electron cloud of tar compounds destabilising their aromatic rings and leading to ring splitting. Using 6 wt.% CaO mixed with coal tar in a fluidised bed gasifier, Yongbin et al., [25] showed that increased CO in the syngas was the result of the cracking of phenolic compounds which is favoured at high temperature. Other groups have observed a decrease in CO production which has been explained by catalysis of the water gas shift reaction. However the data produced in this study consistently showed an increase in CO for each of the quantities of CaO investigated.

Both Boroson et al., [27] and Morf et al., [28] proposed that an increase in concentration of H<sub>2</sub> and CO with the addition of CaO is indicative of the occurrence of secondary tar reactions and according to Xu et al., [29], these reactions can be summarised by Eqs. (1) and (2).



Yongbin et al., [25] also reported that the increase in CH<sub>4</sub> was produced primarily from the cracking of aliphatic hydrocarbons (>C<sub>2</sub>), the rupture of methyl, oxymethylene and polymethylene side chains of aromatic compounds as well as the splitting of ringed compounds. Evidence of ring splitting in this study was observed not only by the reduction in concentration of polyaromatic hydrocarbons (PAHs) but also by the disappearance of dibenzofuran, 3-formyl-2-methyl indole, fluoranthene, pyrene and Class 1 tars.

It can be seen therefore that by mixing CaO into a fixed bed of FCB, it acted as an in situ catalyst cracking primary tars and catalysing secondary tar reactions which resulted in increased production of H<sub>2</sub>, CO and CH<sub>4</sub>. The effects on tar composition and dew point are discussed in the following section.

### 3.2. Tar conversion using in-bed CaO

Also important in the evaluation of the impact of CaO on gasification of FCB is its influence on tar composition and dew point. The tar dew point was calculated as outlined in Section 2.4.4. The data collected on the reduction in tar yield using in-bed CaO also showed that this was associated with a significant change in tar composition and therefore tar dew point. The overall impact of the use of in-bed CaO on tar composition is illustrated in Fig. 4, where it can readily be seen that 3 wt.% and 6 wt.% CaO showed considerable activity towards decomposition of Class 1 and 5 tars. From the data presented in Fig. 4, it is evident that the addition of 2 wt.% CaO resulted in a significant reduction in Class 1, 4 and 5 tars. Class 1 tars were reduced from 10% to less than 4%, Class 4 tars from 21% to less than 10% and

**Table 4**  
Comparison of typical syngas composition with and without the use of in-bed CaO.

Syngas Composition (%)	Without CaO	2 wt.% CaO	3 wt.% CaO	6 wt.% CaO
H <sub>2</sub>	12.1	12.3	13.9	16.5
CO	17.2	18.0	20.9	21.5
CH <sub>4</sub>	3.6	4.1	4.8	5.0

Class 5 tars from 21% to less than 1%. Increasing the percentage content of CaO to 3 wt.% eliminated the production of Class 1 and 5 tars and reduced the occurrence of Class 4 tars to 8%.

However, there was an increase in the occurrence of Class 2 and 3 tars of 28% and 4% respectively. This further supports the observation that CaO promotes tar cracking reactions as discussed in Section 3.1 since cracking and ring opening reactions amongst Class 1, 4 and 5 tars would lead to the production of straight chain compounds and those with fewer rings. Increasing the in bed CaO to 6 wt.% further reduced the Class 4 tars to 5%. This was accompanied by an increase of 23% and 24% in the Class 2 and Class 3 tars respectively. Since Class 5 tars dominate the tar dew point, the absence of these in the tar produced after addition of CaO reduced the tar dew point to 30 °C an overall reduction of 61 °C. Also as there was no evidence of the existence of Class 1 tars with the addition of 3 wt.% and 6 wt.% CaO, the tar dew point calculated represented the true dew point of the tar produced.

The tars which were absent from the samples collected were the 4 ring and larger PAHs, and the overall effect therefore of CaO on tar production here was an increase in Class 3 tars which are the light aromatic 1-ring compounds which pose limited problems with respect to condensability and water solubility (Table 5).

The disappearance of 4-ring and large PAHs was also reported by Yongbin et al., (2004) when CaO was added during gasification of coal tar, and they concluded that this was as a result of rupturing of the PAH ring structures. The data produced provides strong evidence that the increase in syngas yield and in Class 3 tars with the addition of CaO was a direct consequence of decomposition of these large PAHs. Given the increase in H<sub>2</sub>, CO and CH<sub>4</sub>, additional decomposition routes for reduction and change in tar composition are most likely, those proposed by Abu El-Rub et al., [10] which are listed in Eqs. (3) and (4):



where C<sub>n</sub>H<sub>x</sub> represents tar and C<sub>m</sub>H<sub>y</sub> represents hydrocarbons with smaller carbon numbers than C<sub>n</sub>H<sub>x</sub>.

It is widely accepted that the potential for condensation and deposition of tar is dependent on the composition and the chemical properties of the component compounds. According to van Paasen and Kiel, [8] and Li et al., [30] even at concentrations of approximately 0.1 mg Nm<sup>-3</sup> Class 5 tars have a tar dew point of 120 °C which exceeds the dew point at which condensation of Class 2, 3 and 4 tars even at concentrations in excess of 1000 mg Nm<sup>-3</sup> would occur.

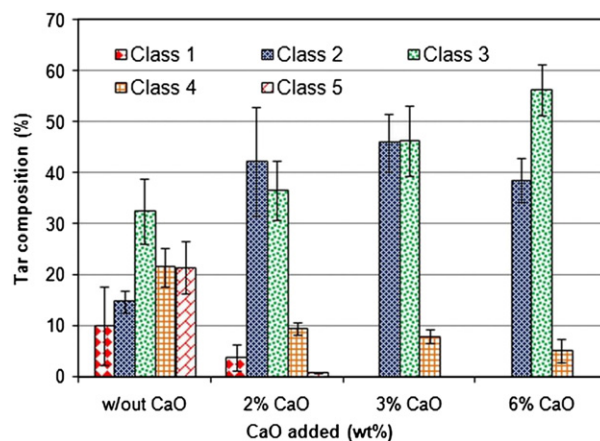


Fig. 4. Effect of varying concentrations of in-bed CaO on tar composition.

**Table 5**

Change in concentration of GC-detectable and gravimetric tars in syngas with increasing concentration of in bed CaO.

Tar class	Classification	Concentration of GC-detectable and gravimetric tars in syngas produced during gasification of fuel cane bagasse (mg Nm <sup>-3</sup> )			
		Without CaO	2 wt.% CaO	3 wt.% CaO	6 wt.% CaO
1	Heavy PAHs 7 or more rings	29.7	17.6	ND	ND
2	Heterocyclic aromatics	14.2	160.9	123.4	56.9
3	Light aromatics (1 ring)	218.4	109.3	107.0	67.1
4	Light PAHs (2–3 rings)	320	33.3	27.4	9.7
5	Heavy PAHs (4–6 rings)	38.8	9.4	2.2	ND
Tar dew point (°C)		90 ± 6	53 ± 8	32 ± 5	30 ± 4

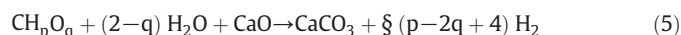
\*ND – Not detected.

Within this context the elimination by 3 wt.% and 6 wt.% in bed CaO of Class 1 and Class 5 tars from the tar was produced during gasification of this feedstock and the significant increase in Class 3 tars therefore represents a considerable change in the potential for tar condensation and deposition during gasification in this system. Furthermore, it has significant implications for the type of syngas cleaning system which will be required for use in an industrial gasification system operating on this feedstock.

Class 3 tars are not known to condense even at concentrations as high as 10000 mg m<sup>-3</sup> and therefore do not play a role in tar deposition [30]. However Class 2 tars which now constitute 35% and 45% after the addition of 3 wt.% and 6 wt.% CaO respectively are now the tars of concern since they will readily undergo condensation and deposition at these concentrations and now dominate the tar dew point. Since the dew point has been reduced to less than 60 °C maintaining the operating temperature of downstream syngas users at temperatures greater than 60 °C would minimise the deposition of these tars on syngas contact surfaces. However a reduction in concentration of these compounds to less than 1 mg m<sup>-3</sup> through the use of existing tar treatment technologies including catalytic cracking and catalytic steam or dry reforming would be more efficient in minimising the condensation of these compounds.

Although granular CaO was mixed manually with FCB pellets the increase in syngas yield and significant reduction of Class 1 and 5 tars suggest that with more effective mixing of CaO and bagasse pellets higher efficiencies of tar conversion should occur. Effective dispersion of CaO in the fuel is essential to ensure maximum catalytic action of the CaO in reacting with the tar species as they are formed. It is expected that incorporation of the CaO during the pelletisation process would provide the most effective means of dispersion of CaO in the fuel. The observations made on CaO show that as a primary measure it is effective at reducing tar yield, increasing syngas yield, increasing syngas LHV and reducing the tar dew point.

Significant hydrogen yield at high CaO loadings (CaO/Carbon = 2) during anaerobic gasification of sawdust has been observed by Han et al., [31]. It is likely that part of the observed hydrogen yield enhancement shown in Table 4 can be the result of the direct biomass reaction with CaO in the pyrolysis zone of the reactor according to the reaction [31]:



in which biomass is modelled as CH<sub>p</sub>O<sub>q</sub>. However, we have not analysed the contribution of the above reaction to hydrogen enrichment compared with the hydrogen generation through the catalytic cracking of tars.

## 4. Conclusions

This work represents the first published data on the effect of CaO on tar production in a pilot scale downdraft gasifier. Furthermore unlike laboratory based systems which have investigated single model compounds this investigation has evaluated the tar conversion capacity and overall effect on a complex biomass gasification system. The fuel used in this investigation was selected specifically due to the expected high tar levels as a result of its high lignin content [3,21].

The results show that the tar produced by FCB under optimal gasification conditions is primarily lignin derived tar and is dominated by Class 2 and 5 tars. Additionally 10% of the total tar produced is comprised of Class 1 tars and as a consequence the true tar dew point is higher than the calculated average value of 90 ± 6 °C. It has also been shown that a reduction in the true tar dew point to between 30 and 32 °C can be achieved through the use of 3 wt.% and 6 wt.% in-bed CaO which catalyses the destruction of Class 1 tars and/or their precursor compounds. Of the three quantities of in-bed CaO used, 6 wt.% of the additive was found to be the most effective at increasing syngas yield, reducing the tar concentration and decreasing the tar dew point.

## Acknowledgements

This work was supported by EU FP7 Integrated Project (COPIRIDE). Andrea Jordan was supported for her PhD studies by a National Development Scholarship from the Government of Barbados and a research grant from the Barbados Light and Power Company Limited which also supplied fuel cane bagasse for the experiments. We are grateful for all the support received.

## References

- [1] C. Higman, M. van der Burgt, Gasification, second ed. Elsevier, Amsterdam, 2008.
- [2] L. Wang, C.L. Weller, D.D. Jones, M.A. Hanna, Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production, Biomass and Bioenergy 32 (2008) 573–581.
- [3] C.A. Jordan, G. Akay, Occurrence, composition and dew point of tars produced during gasification of fuel cane bagasse in a downdraft gasifier, Biomass and Bioenergy 42 (2012) 51–58.
- [4] G. Akay, M. Dogru, O. Calkan, B. Calkan, Biomass processing in biofuel applications, in: P. Lens, P. Westermann, M. Haberbauer, A. Moreno (Eds.), Biomass for Fuel Cells – Renewable Energy from Biomass Fermentation, IWA Publishing, London, 2005, pp. 51–75.
- [5] G. Akay, M. Dogru, O.F. Calkan, Biomass to rescue, The Chemical Engineer 786 (2006) 55–57.
- [6] J. Huang, K.G. Schmidt, Z. Bian, Removal and conversion of tar in syngas from woody biomass gasification for power utilization using catalytic hydrocracking, Energies 4 (2011) 1163–1177.
- [7] C.A. Jordan, G. Akay, Speciation and distribution of alkali, alkali earth metals and major ash forming elements during gasification of fuel cane bagasse, Fuel 91 (2012) 253–263.
- [8] S.V.B. van Paasen, J.H.A. Kiel, Tar formation in a fluidised-bed gasifier – impact of fuel properties and operating conditions, Energy research Centre of The Netherlands (ECN) Report: ECN-C-04-013, 2004.
- [9] L.P.L. Rabou, R.W.R. Zwart, B.J. Vreugdenhil, L. Bos, Tar in biomass producer gas, the Energy Research Centre of The Netherlands (ECN) experience: an enduring challenge, Energy Fuel 23 (2009) 6189–6198.
- [10] Z. Abu El-Rub, E. Bramer, G. Brem, 2004 review of catalysts for tar elimination in biomass gasification, Industrial and Engineering Chemistry Research 43 (2004) 6911–6919.
- [11] L. Devi, K. Ptasiński, F. Janssen, A review of the primary measures for tar elimination in biomass gasification processes, Biomass and Bioenergy 24 (2003) 125–140.
- [12] M. Miskolczi, N. Borsodi, F. Buyong, A. Angyal, P.T. Williams, Production of pyrolytic oils by catalytic pyrolysis of Malaysian refuse-derived fuels in continuously stirred batch reactor, Fuel Processing Technology 92 (2011) 925–932.
- [13] I.F. Elbaba, C. Wu, P.T. Williams, Hydrogen production from the pyrolysis-gasification of waste tyres with a nickel/cerium catalysts, International Journal of Hydrogen Energy 36 (2011) 6628–6637.
- [14] C. Wu, L. Wang, P.T. Williams, J. Shi, J. Huang, Hydrogen production from biomass gasification with Ni/MCM-41 catalysts: influence of Ni content, Applied Catalysis B: Environmental 108 (2011) 6–13.
- [15] P. Simell, N. Hakala, H. Haario, Catalytic decomposition of gasification gas tar with benzene as the model compound, Industrial Engineering Chemistry Research 36 (1997) 42–51.

- [16] A.K. Dalai, E. Sasaoka, H. Hikita, D. Ferdous, Catalytic gasification of sawdust derived from various biomass, *Energy and Fuel* 17 (2003) 1456–1463.
- [17] G. Xu, T. Murakami, T. Suda, Y. Matsuzawa, H. Tani, Y. Mito, Enhanced conversion of cellulosic process residue into middle caloric fuel gas with Ca impregnation in fuel drying, *Energy and Fuel* 22 (2008) 3471–3478.
- [18] Q.-Z. Yu, C. Brage, T. Noordgreen, K. Sjostrom, Effects of Chinese dolomites on tar cracking in gasification of birch, *Fuel* 88 (2009) 1922–1926.
- [19] G. Akay, Renewables come together, *The Chemical Engineer* 786 (2006) 58–61.
- [20] Akay, G., 2012. Ammonia production by integrated intensified processes, International Patent Publication PCT WO/2012/025767.
- [21] G. Akay, C.A. Jordan, Gasification of fuel cane bagasse in a downdraft gasifier: influence of lignocellulosic composition and fuel particle size on syngas composition and yield, *Energy and Fuel* 25 (2011) 2274–2283.
- [22] M. Dogru and G. Akay, Catalytic gasification, European Patent, 1687390 (2006); Australian Patent, 2004–88845 (2010) and Japanese Patent, 2006–53894 (2011).
- [23] CEN/TS 15439:2006, Biomass Gasification — Tar and Particles in Product Gases — Sampling and Analysis, 2006.
- [24] Z. Tingyu, Z. Shouyu, H. Jiejie, W. Yang, Effect of calcium oxide on pyrolysis of coal in a fluidized bed, *Fuel Processing Technology* 64 (2000) 271–284.
- [25] J. Yongbin, H. Jiejie, W. Yang, Effects of calcium oxide on the cracking of coal tar in the freeboard of a fluidized bed, *Energy and Fuel* 18 (2004) 1625–1632.
- [26] W. Torres, S. Pansare, J. Goodwin Jr., Hot gas removal of tars, ammonia, and hydrogen sulphide from biomass gasification tars, *Catalysis Reviews: Science and Engineering* 49 (2007) 407–456.
- [27] M.L. Boroson, J.B. Howard, J.P. Longwell, W.A. Peters, Heterogeneous cracking of wood pyrolysis tars over fresh wood char surfaces, *Energy and Fuel* 3 (1989) 735–740.
- [28] P. Morf, P. Hasler, T. Nussbaumer, Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips, *Fuel* 81 (2002) 843–853.
- [29] G. Xu, T. Murakami, T. Suda, Y. Matsuzawa, H. Tani, Y. Mito, Enhanced conversion of cellulosic process residue into middle caloric fuel gas with Ca impregnation in fuel drying, *Energy and Fuel* 22 (2008) 3471–3478.
- [30] C. Li, K. Suzuki, Tar property, analysis, reforming mechanism and model for biomass gasification — an overview, *Renew Sust Energ Rev* 13 (2009) 594–604.
- [31] L. Han, Q. Wang, Y. Yang, C. Yu, M. Fang, Z. Luo, Hydrogen production via CaO sorption enhanced anaerobic gasification of sawdust in a bubbling fluidized bed, *International Journal of Hydrogen Energy* 36 (2011) 4820–4829.