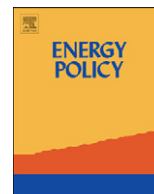




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Sustainable gasification–biochar systems? A case-study of rice-husk gasification in Cambodia, Part I: Context, chemical properties, environmental and health and safety issues

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ABSTRACT

Biochar is a carbon- and energy-rich porous material produced through slow pyrolysis of biomass, which has been proposed as a way of storing carbon in soils for the long-term (centurial to millennial timescales) but its production incurs an energy penalty. Gasification of rice husks at paddy mills combines the benefits of reasonably efficient delivery of energy with a reasonably high carbon char and ash mixture. The ca. 35% carbon content of the rice husk char is possibly a consequence of the protective shield of silica, preventing full exposure of the biomass to oxidation in the gasifier. In this paper we undertake an evaluation of the sustainability of this 'gasification–biochar system' (GBS) in Cambodia, where a rapid deployment of gasifiers is underway. In Part I, we describe the context and analyse (some of) the physical and chemical properties of the biochar. While there are some potential health, safety and environmental issues that require further analysis, they are problems that could be readily addressed in further research and appear to be resolvable. In Part II, we present results from field trials, summarise the data on the carbon abatement of the gasification–biochar system and present some preliminary economic data.

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1. Introduction

There has been much recent interest in biochar as a way of stabilising photosynthetic carbon, usually with associated energy by-products (syngas, bio-liquids and/or heat) (Lehmann and Joseph, 2009; Shackley and Sohi, 2010; Sohi et al., 2010; Verheijen et al., 2009). Biochar has been defined as 'the porous carbonaceous solid produced by thermochemical conversion of organic materials in an oxygen depleted atmosphere which has physiochemical properties suitable for the safe and long-term storage of carbon in the environment and, potentially, soil improvement' (Shackley and Sohi, 2010). The technology that is most frequently discussed for producing biochar is pyrolysis, specifically slow pyrolysis, because this produces a higher biochar yield than other conversion technologies (ca. 35%) (Brownsort, 2009). However, an unfortunate side-effect of a high biochar yield is that the delivered energy yield is lower, this being a consequence of the high energy value (ca. 25–30 MJ kg⁻¹) of the

biochar product. Hence, if the main purpose of a development is energy generation, rather than carbon abatement, then a more efficient technology in terms of delivering useable electricity or heat or both is probably preferable to slow pyrolysis, such as fast pyrolysis or gasification (Hammond et al., 2011) (both with a char yield of ca. 10% or less) (Bridgwater, 2007).

Biomass gasification has been developed in developing and industrialising countries with companies such as Ankur Scientific Energy Technologies Pvt. Ltd. (based in India) manufacturing a range of gasifiers from a few kW to hundreds of kW capacity (<http://www.ankurscientific.com/>). Ankur has sold over 1000 gasification units, predominantly in South Asia, but also into Africa, Europe, South America and SE Asia. The char from such gasifiers is sometimes used as a fuel, where the calorific value (CV) is sufficiently high (e.g. > 15 MJ kg⁻¹). Where rice husks are used, however, the high silica content limits the CV of the rice husk char (RHC) (e.g. to ca. 8.5 MJ kg⁻¹ (Nagori, 2010)), hence it has less value as a charcoal-type fuel and the RHC can become a waste disposal or pollution problem. In these circumstances, it may make sense to regard the RHC as a form of biochar and to apply to agricultural soils to enhance crop yields and soil 'health'. This was the motivation behind the BIOCHARM project (Biochar for Carbon Reduction, Sustainable Agriculture and Soil

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Management), supported by the Asia Pacific Network on Global Change (APN) and by the UK Biochar Research Centre (Karve et al., 2010).

Very large quantities of rice husk are produced globally every year—ca. 120 mt (20% of total rice production) and these frequently become a waste problem or are burnt as a fuel (Bronzeoak, 2003). It is estimated that ca. 20 mt of rice husks find an application per year (Ankur, 2010), suggesting that very large quantities become a waste. On the other hand, increasingly large amounts of rice husks are finding a use as a bio-fuel in combustion units for electricity (and, to some extent, heat) generation and prices of ca. \$30 t⁻¹ have been reported in Thailand and parts of India (e.g. Andhra Pradesh state) (Parnphuneesup and Kerr, 2011). Open-burning of rice husks, once a common practice in rice-growing countries, is much less common in some areas because of the new markets for husks. Estimating the availability of 'waste' (i.e. zero or very low cost) rice husks is difficult due to the dynamic and spatially specific markets for rice husks.

Considerable effort has been devoted to finding applications for rice husk ash produced from combustion and existing markets are as an insulator in the production of high quality flat steel and as a pozzolan in the cement industry; there is a range of smaller-scale applications (water filtration and purification, as a soil amendment, an absorbent of oil and other contaminants, as a way of protecting foods from pests, etc.) (Bronzeoak, 2003; Foo and Hameed, 2009). Some proportion of rice husk ash appears to have a similar carbon content to RHC (35%), presumably the result of oxygen-depleted 'combustion', but the typical commercial rice husk ash usually has a maximum of 5–7% carbon content (Bronzeoak, 2003).

In order to ascertain whether gasification and production of RHC are sensible and effective uses of resources we have developed criteria for defining a sustainable biochar system and endeavour in this study to apply these criteria to the rice husk gasification system in one country – Cambodia – which has experienced a rapid uptake of rice husk gasification since about 2006. Cambodia is an important rice producer, with 6–7 mt yr⁻¹, generating some 1.5 mt of husks.

A *sustainable biochar system* can be defined as one, which (a) produces and deploys biochar safely and without emitting excessive non-CO₂ greenhouse gases, (b) reduces net radiative forcing, (c) does not increase inequality in access to and use of resources and (d) provides an adequate return on investment. Condition (a) is important to ensure that new technologies and practices do not pose undue risks to human health and safety and the environment (e.g. through inhalation of dust and dangerous crystalline particles, biochar particles turning waterways or surrounding vegetation 'black', dispersion of potentially toxic chemicals such as tars containing polycyclic aromatic hydrocarbons (PAHs), adding N₂O, CH₄ or black carbon and soot particles to atmosphere increasing net greenhouse forcing, etc.) (Lai et al., 2009; Ramanathan and Carmichael, 2008; Tipayarom and Oanh, 2007).

Condition (b) is important to ensure that the net result is indeed to reduce net radiative forcing relative to a baseline case (primarily through reduction in atmospheric concentration of greenhouse gases through removal and avoided emissions). Condition (b) also takes account of direct and indirect land-use changes (I/LUC), which can result in one-off emission of large amounts of carbon, e.g. hundreds of tonnes per hectare in the case of tropical and peatland rainforest (Fargione et al., 2008; Searchinger et al., 2008). Clearing of Brazilian wooded *cerrado* is estimated to incur a one-off carbon loss of ca. 45 t C ha⁻¹, US grassland ca. 30 t C ha⁻¹ and abandoned US crop land zero or only a few tonnes per ha (Searchinger et al., 2008). Clearly, there is no point in converting land that incurs a large loss of carbon to biomass production for energy if the main (or a large part

of the) rationale of a project is to abate carbon through biochar production.

Condition (c) is relevant because an increase in demand for biomass will have knock-on impacts upon other users or potential users of that (or other) biomass, demand for which increases due to substitution effects. This also relates to LUC and ILUC, which frequently encounters equity and justice problems and questions. Condition (d) refers to economic viability since in market economies investment will only follow favourable rates of return. Defining an 'adequate rate of return' is fraught with difficulties and depends upon subjective considerations such as the discount rate selected.

1.1. Structure of the paper

In Part I we present information on the deployment of the gasification technology in Cambodia, including the delivered energy outputs, the yield of RHC, the carbon balance, the conservation of elements within the biochar, the labile carbon content, the recalcitrant carbon fraction and some other properties of the RHC. Part I will also consider potential environmental contaminants and potential health risks arising from deployment of RHC. We consider only the application of the solid RHC, not of combinations of the RHC with other waste streams such as the 'black water' and sludge from the settling ponds. At some facilities, it appears that such liquid wastes have been added to RHC prior to field application: this raises environmental pollution and health concerns that are not addressed here.

In Part II, we describe the utilisation of RHC in agricultural systems, including transportation, application to field and preliminary findings on impacts on crop yields. We also undertake a simple economic assessment from the perspective of CO₂ equivalent emissions and pull together information from Parts I and II to draw the key conclusions.

2. Characterisation of the gasification technology installed in Cambodia

As of mid-2010, approximately 35 Ankur Scientific Ltd. (India) gasification units had been installed in Cambodia by SME Renewable Energy Ltd., a Cambodian company, which acts as a turnkey project developer and financier. The gasifier units are typically rated from 150 to 350 kW_e in delivered power capacity. Most are installed in rice mills and ice-making factories. Paddy rice milling separates the rice kernel from the surrounding husk. The husks typically constitute 22% of the paddy rice pre-milled weight. Approximately 1/3 of the husk produced by the milling process is required to fuel the gasifier. Gasification of the biomass occurs at 900–1100 °C. The gasification temperature is determined by the fuel–air ratio entering the reactor but this is not strictly controlled. There are, furthermore, other factors influencing the precise temperature that are outside of operator control (such as humidity and the physical and chemical composition of the biomass). For these reasons it is not possible to operate the gasifiers in a very narrowly prescribed range of temperatures (Nagori, 2011, pers. com.) and the gasification temperature is likely to vary with the load of the system.

The technology supplier indicates that 1.6–1.8 kg husk is required per kWh of power produced. We have assumed a value of 1.7 kg husk kWh⁻¹. The resulting syngas or producer gas is cleaned through a series of coarse wire filters (containing rice husk char in 3–5 mm size range), fine wire filters (containing saw dust in size 0.5–3 mm range) and cloth filters and is introduced into a normally aspirated diesel engine, (200–350 hp) where it is combusted. The engine provides either mechanical or electrical

power used to operate the milling machinery. A schematic diagram of the process is illustrated in Fig. 1 while information for several different operational gasifiers is presented in Table 1.

The syngas produced by the gasification of rice husk can reduce the consumption of diesel fuel by 70–75%. Since diesel fuel cost constitutes up to three quarters of the direct operational costs of operating a rice mill, the rapid increase in diesel costs that has occurred in the mid- to late-2000s has been an important driver in accelerating installation of gasification units. A typical 1 to 2 t h⁻¹ rice mill can save \$4000–\$6000 per month in diesel fuel expenses through using rice husk gasification technology with total equipment and civil works costs of about \$85,000. Therefore, a gasification unit can pay back the investment cost in fuel savings

in less than two years. The economics of installing Ankur gasifiers make sense in the Cambodian context for a few distinct reasons:

- Cambodian rice mill energy needs are usually less than 1 MWh electric (e). This requirement is relatively small and installation of husk fuelled boilers with steam turbines would not be feasible at this scale (small steam turbines not being very reliable or efficient);
- the electricity grid is poorly developed in Cambodia, hence micro-grid and own supply solutions are cost-effective, where this might not be the case in a centralised grid-connected situation;

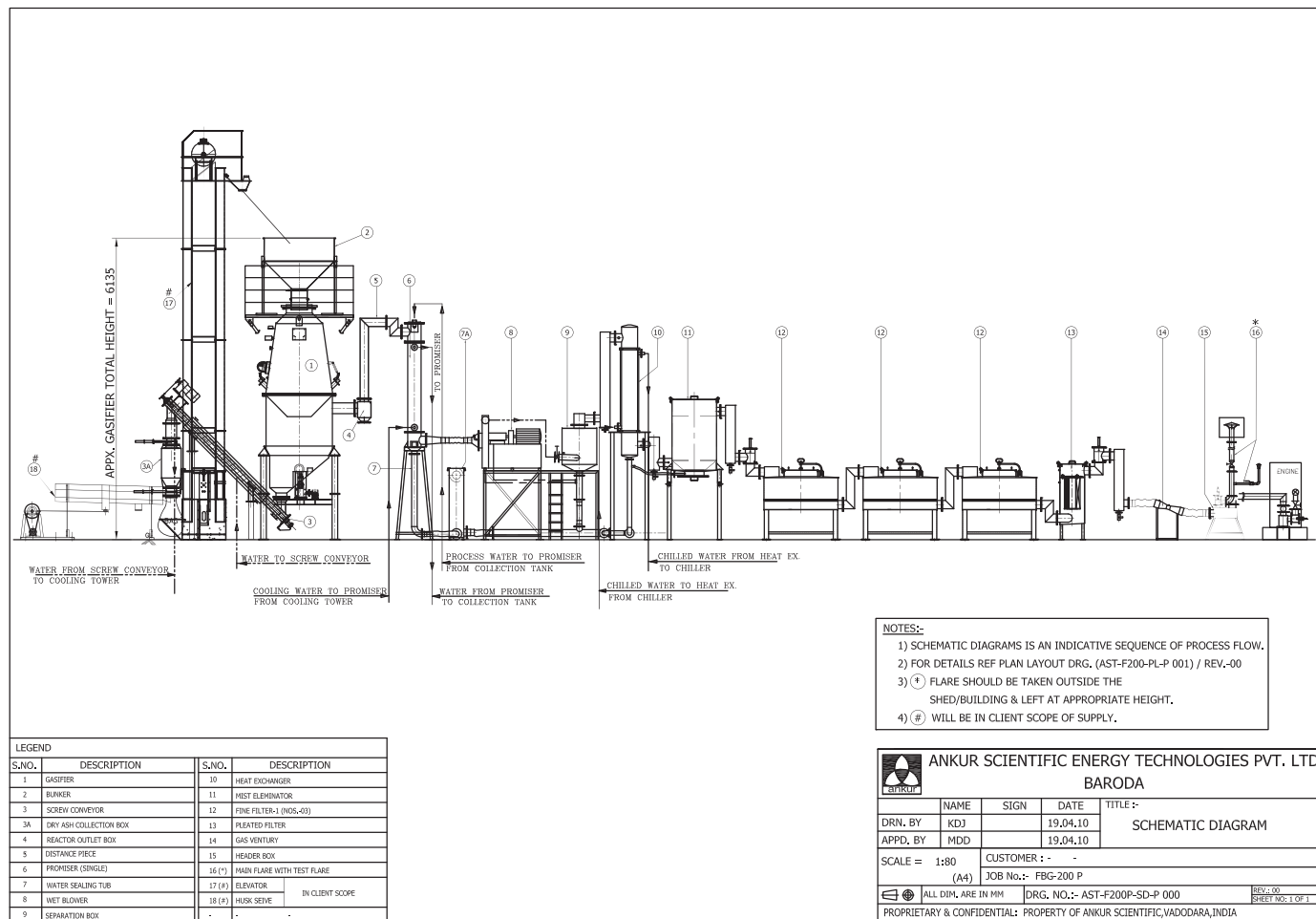


Fig. 1. Design of Ankur Scientific Pvt. Ltd. Rice Husk Gasifier (source: the company).

Table 1

Characteristics of six gasifiers installed in Cambodia by SME Renewable Energy Ltd.
Source: SME Renewable Energy Ltd.

Gasifier ID	Installation date	kWe	Diesel fuel saved (litres yr ⁻¹)	Running h yr ⁻¹	% Total hours	Fuel replacement (litres h ⁻¹)	Avoided fossil fuel emissions (t CO ₂ yr ⁻¹) ^a
1	06.08	200	75,240	3960	45	19.00	199
2	11.08	200	91,080	3960	45	23.00	240
3	01.09	200	165,600	7200	82	23.00	437
4	01.09	200	71,280	3960	45	18.00	188
5	11.07	150	165,600	7200	82	23.00	437
6	08.08	250	110,880	3960	45	28.00	293

^a Assumes a carbon emissions factor of 2.6391 kg CO₂ per litre (Defra, 2009).

- even where grid-connection exists, electricity supply in Cambodia is not subsidised as it is in some other countries, hence renewables can compete on a more level playing field with fossil-fuel fired electricity generation.

It also appears that there is less competition for rice husks as a fuel in Cambodia compared to the situation in other countries, where there is a better developed biomass fuel supply chain and infrastructure.

From the ECN Phyllis database (<http://www.ecn.nl/phyllis/>) the lower heating value (LHV) of rice husk is around 12–15 MJ kg⁻¹ and we assume here a value of 13 MJ kg⁻¹.

Therefore, ca. 22 MJ (6.1 kWh) in the fuel is used to produce 1 kWh, implying an efficiency of ca. 16%. While this is a lower efficiency than modern gasification technologies (ca. 25–35+%) (Peacocke, 2011), given the abundance of the local feedstock, (cost free for the rice mill), at the gasifier site, and the overall favourable project economics, it does not detract from the value of the technology though it can be argued that the farmer should be receiving something for providing the rice husks, which after all have a value, and this would affect project economics) (Parnphuneesup and Kerr, 2011).

The gasification process generates tars, which drop down into barrels below the gasifier and also below the several-stage gas filters. Water is used for quenching the syngas and removing tars in a scrubber producing a 'black water' containing some condensates. This same black water is then used for quenching and removing the RHC from the base of the gasifier. The black water is then conveyed to a cooling 'shower' device and a settling pond before being reintroduced into the scrubber. At one mill, the black water is replaced on a weekly basis; water treatment works are not generally available. There is a risk that some of the dirty water stream may seep into the ground and ultimately into local water courses or the water table. A preliminary analysis of the waste water has been undertaken as part of this study in order to better understand the potential pollution risks if the black water should seep into the ground.

3. Rice husk char yield and physico-chemical properties of RHC

The char yield from rice husks is ca. 35% and the carbon content of the char is ca. 35% (own analysis). Knoblauch et al.

(2010) present a higher carbon value of 43% in RHC; the reason for the difference is not known but could be methodological. Therefore, for each tonne of rice husk gasified, 350 kg of RHC is produced containing 123 kg C or 451 kg CO₂. The carbon content of the rice husks is about 38% (own analysis), therefore 32% of the carbon in the feedstock is conserved. This is much higher than the typical value for gasification of 2.5–8% carbon conservation. Table 2 presents information on the tests conducted on the biochar samples and the analytical methods used. Table 3 provides information on the composition of a range of rice husk samples and corresponding RHC.

Rice husk contains approximately 20% ash, the main constituent of which appears to be silica; the carbon content of rice husks at 38% is lower than typical biomass (ca. 50%) due to the high ash content. The RHC is largely made up of silica and carbon—just over 60% ash to 35% carbon. Other measurements of the ash content are higher (e.g. at 72.5%) (Nagori, 2010).

The high silica content of the rice husk may help explain why the conversion of organic carbon to CO₂ is much lower for rice husk than in the case of gasification of other biomass. The exterior of rice husks is composed of dentate rectangular units, which may form a geometric shield, which protects the combustible material, 'cocooning' the carbon such that air circulation is reduced (see Fig. 2) (Bronzeoak, 2003). Fig. 3 is a 3-D image of the rice husk char, which provides evidence that the organic matter may enjoy considerable protection from the harsh conditions in the gasifier. According to one study, the role of silica is "more than just a geometric shield to the combustible material in the sample" and that silica "forms molecular bonds with carbon, which are not easily broken at the gasification temperatures" (Bharadwaj et al., 2004, pp. 985–986). Silicon carbide is not formed since this entails much higher temperature reactions (2500 °C) than occur in gasification. From a carbon storage perspective, this feature of rice husk gasification is fortuitous, as it combines the benefits of gasification for electricity generation with carbon conservation that is over 50% of that achieved through slow pyrolysis (50–55% of the carbon in the feedstock is typically conserved within the biochar produced by slow pyrolysis) (Lehmann and Joseph, 2009).

The measure of volatiles in rice husks in Table 3 shows that ca. 39% by mass is non-volatile recalcitrant material (e.g. silica and recalcitrant carbon). This is a slightly higher yield than RHC, presumably because the gasification exposes the rice husks to more extreme conditions. On the other hand, the

Table 2
Set of analytical tests and methods undertaken in analysis of the RHC.

Test	Variables measured	Measurement unit	Details of tests	Laboratory undertaking test
pH	pH	pH units	Electrochemical	SETN
Moisture	Moisture	% Of fresh mass	1. 105 °C for 48 h (oven-dry) 2. Thermogravimetric	UKBRC SETN
Loss on ignition (LOI)	Non-ash content	% Of fresh or oven-dry mass	Thermogravimetric	SETN
Ash	Ash content	1—LOI	Deduction	N.A.
Elemental analysis	C, H, N, S	% Of oven-dry mass		SETN
Exchangeable cations	K, Na, Ca, Mg	c mol kg ⁻¹ (dry weight)	ICP-OES	SETN
Cation exchange capacity (CEC)	Sum of above	c mol kg ⁻¹ (dry weight)	ICP-OES	SETN
Metals and other elements (total)	Al, As, Ba, Be, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Zn, Hg, B, Ca, Co, Fe, K, Mg, Mn, Na, Si, V, Sr, Ti	mg kg ⁻¹ (dry weight)	Combustive ashing at 750 °C followed by extraction with aqua regia; ICP-OES	SETN
BETX	Benzene, ethylethylene, toluene, xylene	mg kg ⁻¹ (dry weight)	HS-GC-MS	SETN
Phenols	Phenols	mg kg ⁻¹ (dry weight)	GC-MS	SETN
PAHs	16 USEPA PAHs	mg kg ⁻¹ (dry weight)	Extraction with DCM-acetone; ASE, GC-MS	SETN

SETN—Scottish Environmental Technology Network.

Table 3

Properties of Rice, Rice Husk and Carbonised Rice Husk

Source: own analysis, except for column 4, from RENEW (2004), undertaken at SETN laboratories, University of Strathclyde (www.setn.org.uk/) (Anderson, 2009).

Measurement 4 (all dry weight)	Rice (grain and husk) (1 batch)	Rice husk (average 3 batches and/or range shown)	Rice husk (data from RENEW, 2004 with other values in literature in brackets)	Rice husk char (average up to 4 batches, 3 of which match the husks)	Conservation of element from husk to husk char (%) (assuming 33% yield)
Ash (wt%)	6.5	21 (19.8–23.5)	18 (21)	63 (58–67) (72.5) ^a	
C (wt%)	41	38 (36.4–38.9)	44.5 (41)	35 (28.8–36.2) ^b	30
H (wt%)	6.5	4.7 (4.1–5.1)	6.3 (4.3)	0.17 (0.04–0.39)	1.2
N (wt%)	1.4	1 (0.9–1.1)	0.9 (0.4)	0.7 (0.63–0.94)	23
S (wt%)	0.1	0.04 (0.03–0.06)	0.6 (0.01)	< 0.03	41
Volatiles (wt%)			66 (64)	3.8 ^a	
Fixed carbon (wt%)			17 (16)	23.6 ^a	46
Calorific value (MJ kg ⁻¹)			15.7–16.3	8.4 ^a	
pH	6.6	6.6 (6.5–6.8)		9.63 (7.8–10)	
Bulk density (kg m ⁻³)				180 ^a	
Cation exchange capacity (c mol kg ⁻¹)				45–110	
Exchangeable K (c mol kg ⁻¹)				11–72	
Exchangeable Na (c mol kg ⁻¹)				1–21	
Exchangeable Ca (c mol kg ⁻¹)				4–15	
Exchangeable Mg (c mol kg ⁻¹)				1–13	
PAHs (USEPA 16) (mg kg ⁻¹) ^c	0.09	0.23 (0.04–0.37)		15–104	
BETX (mg kg ⁻¹) ^d				7.7–22.3	
Metals and other elements: (all mg kg⁻¹)^e					
Aluminium (Al)	57	37–68		92–543	82–315
Arsenic (As)	< 1.44	< 1.52– < 2.5		< 1.79– < 2.5	
Barium (Ba)	5.7	3–12		19–48	53–127
Beryllium (Be)	< 2.89	< 3.03– < 3.85		< 3.59– < 5.00	
Boron (B)	2.14	4.97–9.35		1.81–5.38	6–29
Cadmium (Cd)	< 0.29	< 0.3– < 0.39		< 0.36– < 0.5	
Calcium (Ca)	250	389–625		609–1940	52–103
Chromium (Cr)	< 1.44	< 1.21– < 3.03		< 1.44– < 2.5	
Copper (Cu)	5.11	1.2–5.2		8.2–15.3	98–297
Iron (Fe)	48	64–67		66–107	40–56
Lead (Pb)	< 1.44	< 1.52– < 1.93		< .32–28.2	
Magnesium (Mg)	827	187–371		162–658	29–59
Manganese (Mn)	75.1	125–315		135–470	25–56
Mercury (Hg)	< 1.44	< 1.52– < 1.93		< 1.79– < 2.5	
Nickel (Ni)	< 0.87	< 0.89–1.95		< 1.39–1.5	
Potassium (K)	2604	1923–3040		595–2418	10–27
Silicon (Si)	5.8	3.2–26.8		66–199	209–340
Sodium (Na)	152	62–141		76–650	36–348
Strontium (Sr)	1.13	0.82–2.50		1.87–9.10	76–159
Titanium (Ti)	0.81	0.33–1.21		1.79–5.25	49–537
Zinc (Zn)	22.4	9.84–20.9		11.7–44.2	27–70
Vanadium (V)	< 1.44	< 1.52– < 1.93		< 1.75– < 2.5	

^a Measurement by Dr. G.P. Nagori, Ankur Scientific Energy Technologies Ltd. (Nagori, 2010). Also RENEW (2004).^b Some values in the literature are somewhat lower, e.g. 24.4% in ECN Phyllis database.^c Polycyclic aromatic hydrocarbons (PAHs).^d Benzene, ethylbenzene, toluene, xylene (BETX) analysed used HS-GC-MS.^e Metals analysed using ICP-OES.

protection of the carbon in the biomass helps to account for the low efficiency in converting the rice husks into delivered energy.

4. Conservation and accumulation of elements in biochar

The conservation of an element in the char is calculated by the following formula:

$$\text{ConsA} = \frac{\text{CharYield} \times \text{CharA}}{\text{FeedstockA}} \quad (1)$$

where ConsA is the proportion of element A retained in the char from the feedstock, CharYield is the mass of the char divided by the mass of the feedstock, CharA is the proportion of element A within the char and FeedstockA is the proportion of element A within the feedstock.

While the metals in Table 3 are shown in elemental form, in reality they are present as oxidised or otherwise compounded species as in the feed. It is possible that some metals are also introduced from the equipment itself as a consequence of abrasion as the feedstock and by-products flow through the process. The metals so introduced would be primarily Fe, Cr and Mn and the amounts would be expected to be extremely low (otherwise the production unit would not last very long). Table 3 does not indicate an excess of those particular elements relative to other metals, so we have assumed in this analysis that the metal contribution from equipment can be ignored. It is also likely that soil particles are introduced with the rice husks and contribute to the results in Table 3.

It can be seen that most of the hydrogen and 80% of the nitrogen are lost during volatilisation. This is more than estimates of N loss in other studies, including of RHC, e.g. (Knoblauch et al., 2010). More of the sulphur (40%) is retained, but slightly less

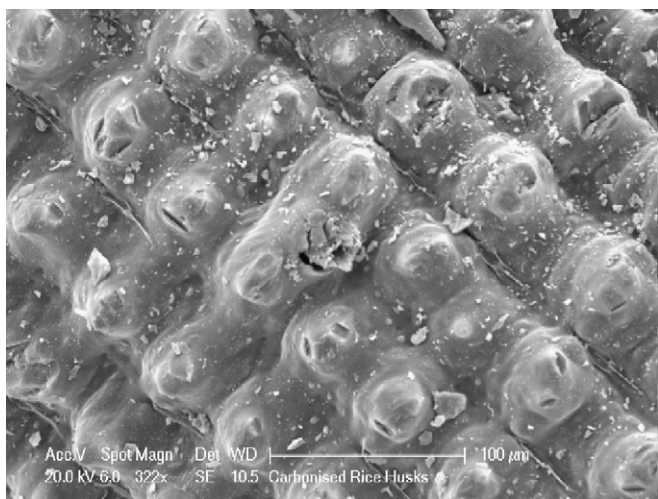


Fig. 2. Scanning Electron Micrograph (SEM) of rice husk char, showing the intact structure of the external silica shell.

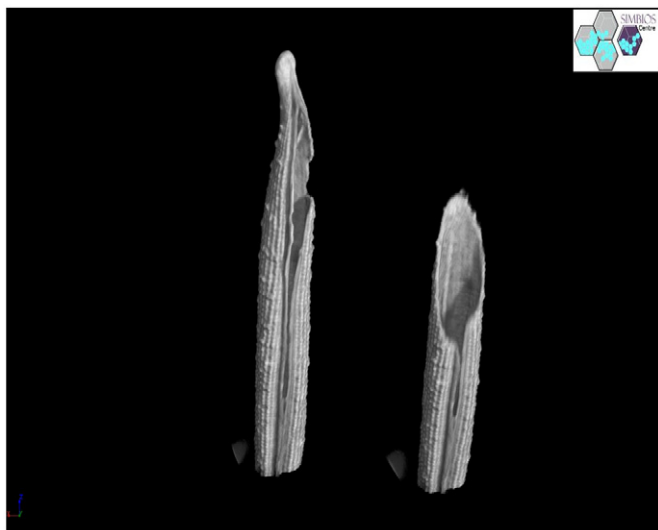


Fig. 3. Three-dimensional image of rice husk char (courtesy of Wilfred Otten, University of Abertay, Dundee).

than reported in other studies (Chan and Xu, 2009). The C/N ratio is 58, comparable to the mean value of 67 in char tested by Chan and Xu (2009). As for the metals, the calculation of conservation for three gasifiers, for which the rice husk and RHC were matched, produced some hard-to-interpret results. The total K concentration is low compared to a range of biochar samples (Chan and Xu, 2009) and is much lower than the value in Knoblauch et al. (2010) (by a factor of 5 to 20 times), for reasons that are not currently known. The gasification temperature operates quite closely to the boiling point of K, however, and slight variations in process conditions might result in large differences in the proportion retained and lost.

The combustive ashing method does not measure totals (contra dry ashing) hence the values in Table 3 may be incomplete with some proportion of the element remaining insoluble thus 'unmeasured', and giving the false impression it has been 'lost'. This could be the case even though the same method is used for the husk and the RHC because of changes in shielding or chemical binding of elements resulting from charring.

For some gasifiers and some elements, the percentage conservation was over 100%. The char yield of each unit from which the char was obtained for analysis has not been calculated but has been assumed at 33% in Eq. (1). Empirical measurements on several gasifiers has shown that the yield can be lower than 33%, however, with values ranging from 10% to 35%. If the yield is less than 33%, then the percentage conservation of elements will be reduced, which would make better sense of the data.

If this was the only explanation, the conservation levels might be expected to be similar across elements, which they are not. Higher percentage conservation levels are evident for copper, silica, sodium, strontium and titanium. There are marked differences between the three gasifiers, especially in comparing gasifier 3 with gasifiers 1+2, which may be due in part to difference in char yield; there is, though, some evidence of a tendency to retain and accumulate particular elements as shown in Fig. 4.

The temperature of the gasifier is above the melting point of certain metals, such as Zn, Cd, As, Se, K, Na and Mg and it might be assumed that volatilisation of these metals will reduce their concentration in biochar since they will disappear in emissions or in tarry effluents (<http://www.chemicalelements.com/show/boilingpoint.html>). Fig. 4 does show that the conservation of Zn, K and Mg is lower than for other metals, indicating possible volatilisation.

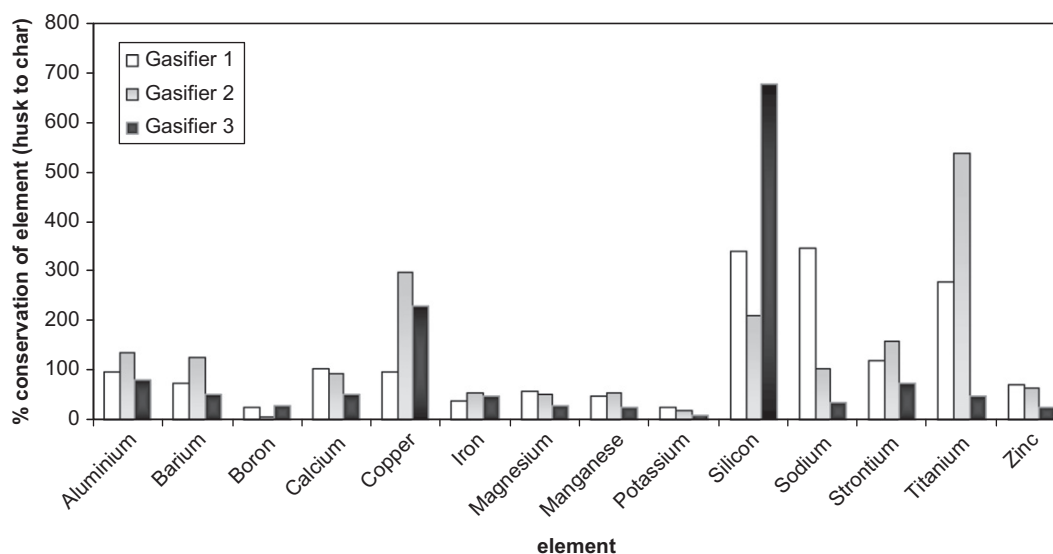


Fig. 4. Retention and accumulation of a range of elements in carbonised rice husks relative to the rice husk feedstocks for three gasifiers (data Table 3).

Na concentration in char, on the other hand, shows a varied response. One study found that about 50% of the Na is lost by vaporisation when heated to 673 °C (Chan and Xu, 2009). Furthermore, levels of metals with much higher boiling points such as B, Fe and Mn also appear to show lower levels of conservation, whereas these metals ought to be conserved. There is evidence of accumulation of metals within the sludge that collects in the settling pond (Karve et al., 2010). This includes metals, which are not fully conserved in RHC such as B, Fe and Mn so it is likely that these elements are transferred by the black water and accumulate in the sludge fraction. Very high concentrations of elements are found within the sludge, especially for Sr, Si, Ca and Ti, all of which have high boiling points, hence are unlikely to be volatilised and removed from the reaction in the gas stream.

Beyond RHC yield differences, this retention and accumulation process might have occurred through the circulation of the water used for gas cleaning and then for quenching and removing the RHC from the bottom of the reactor. Elements may have been removed from the hot syngas when it reacts with water in the gas scrubber, into which the hot syngas from the reactor enters, as well as when water quenches the hot RHC. These elements may then be dissolved into, sorbed or otherwise carried within particles or sediments in the cooling water, only to be adsorbed back into the RHC at a later stage. Where there is a tendency for the elements to be leached out of the char, we would expect retention rates to be lower. This appears to be the case for B, Fe, Mg, Mn, K and Zn. Where a stronger bond develops between the biochar and the element, retention and concentration within the char may result, e.g. for Ba, Ca, Cu, Si, Na, Sr and Ti. Data on the metal concentrations of the black-water before and after change-over of the water (after approximately one week) are partly consistent with the evidence from the metal content of the RHC. Fe, Mg, Mn and K were all found to be higher in the 'old' black-water stream compared to their levels in the newly replaced water stream, consistent with the observation that these same elements have a higher tendency to leach out of char than other elements. One interpretation of the data is that the elements with the lower retention rates are those more readily leached-out of the biochar when it is applied to soils. (Beesley et al. (2010) results using a wood char do not appear to show the same properties as the RHC. In their case, the biochar sorbed Cd and Zn, but not As and Cu. We found that the RHC tend to sorp Cu more than Zn.)

The cation exchange capacity (CEC) of RHC varies from 44 to 110 c mol+kg⁻¹, generally higher than values reported for charcoal, likely to be explained by the high levels of ash in the RHC compared to wood char. The variation in the value of the CEC may be partly explained by the uncertain impact of the cooling water. This may also account for the variation in pH for five RHC biochar samples, from 7.79 to 9.97. Clearly, there is significant variability in the composition of the RHC due to the specificities of the gasification technology and the variable char yield. This makes deriving an accurate estimate and interpretation of the physico-chemical properties of RHC difficult.

5. Labile carbon content and long-term stability of the RHC carbon

There are (at least) four carbon fractions within biochar: (a) super-labile, which mineralises to CO₂ within the short term (hours to a few days); (b) labile, which mineralises over the medium-term (e.g. weeks to months); (c) unstable, which mineralises over the long-term (from months to years); (d) recalcitrant/ fixed, which remains non-mineralised in the long-term (e.g.

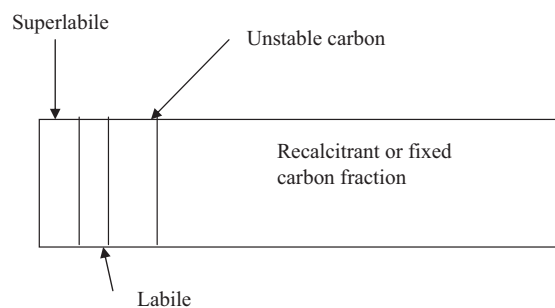


Fig. 5. Diagrammatic representation of the potentially different carbon fractions within biochar (still partly speculative).

> 100 yr). This can be demonstrated diagrammatically in Fig. 5. Mineralisation occurs through microbial and/or abiotic decomposition. The Carbon Stability Factor (CSF) is defined as the proportion of the total carbon in freshly produced biochar, which remains as recalcitrant carbon over a defined time period as defined (Eq. (2)). A CSF of 0.75 means that 75% of the carbon in the fresh biochar remains as recalcitrant carbon over the defined time horizon and that 25% of the carbon has been converted into CO₂:

$$CSF = 1 - C_{lab} - C_{unstab} \quad (2)$$

where C_{lab} is the fraction of carbon that is superlabile and labile and C_{unstab} is the fraction of carbon that is unstable as determined by accelerated ageing methods.

The super-labile and labile content of the RHC was measured using an inoculation technique (Cross and Sohi, 2011). The labile content is ca. 0.36% of the carbon fraction. The recalcitrant carbon fraction refers to that proportion, which is stable and resists microbial and abiotic decomposition in the long-term (decadal to centennial), hence is the one that is relevant to carbon abatement.

The recalcitrant fraction has been measured by an accelerated ageing technique (Masek et al., 2011). The preliminary method used suggests that 7% of the carbon in the biochar is unstable in the long-term. Therefore the recalcitrant fraction is estimated to be ca. 92%. The limitation of this method for calculating recalcitrant carbon is that it has yet to be calibrated against historical charcoal samples. (The accelerated ageing method provides a (ca. 20%) higher recalcitrant carbon value than the 'fixed' carbon method shown in Table 3.)

6. Potential contamination of soil as a consequence of the application of RHC biochar

Up to this point we have considered the effect of the production process as a source of contamination of the solid char residue. We now turn our attention to the potential for RHC to be a source of contamination if it was to be used as a soil amendment. There are two types of contamination in RHC that need to be considered: potentially toxic elements (PTEs), in particular metals; potentially toxic organic compounds (PTOCs). In order to evaluate contamination from PTEs, we have used the UK sewage sludge regulations, which provide a maximum permissible concentration of PTE in soil in mg kg⁻¹ dry solid and a maximum permissible average annual rate of PTE addition over a ten year period (kg ha⁻¹) (DOE, 1996). No equivalent regulations are available for the Cambodian context and we have used the UK guidance in lieu of anything more appropriate. The values are pH dependent and we have used the lowest values where there is a choice to err on the side of caution. Likewise, we have used the highest values for the PTEs from the five RHC samples analysed. The analysis shows that the PTEs in the RHC (Table 3) do not exceed the levels recommended by the UK government.

The element, which is closest to the threshold, is copper but even in this case it would be necessary to add 129 t of RHC ha⁻¹ yr⁻¹ to exceed the threshold.

In respect of the organic contaminants, the main molecules of concern are the polycyclic aromatic hydrocarbons (PAHs), some of which are carcinogenic (Garcia-Perez, 2008; Lerda, 2009). The USEPA 16 PAHs were measured using an accelerated solvent extraction (ASE) and the concentrations in RHC were from 15 to 104 mg kg⁻¹. The detailed speciation of the PAHs is shown in Table 4. Totals were calculated for the 16 PAHs in the case of four RHC samples, while individual concentrations were calculated for a single sample (which has a \sum 16 PAH value of 35 mg kg⁻¹).

There is, as yet, little guidance available on the appropriate limits for PAHs in soil amendments and few regulatory agencies have attempted to define quantitative thresholds to date. One of the few exceptions is the Flemish regulatory authority in Belgium, which has defined quantitative limits expressed in terms of mg kg⁻¹ in material to be added to soils (Ruyschaert and Nelissen, 2010).

There is data on existing PAH levels in soils and this indicates that levels can vary considerably between locations and soil types. In the UK, the range for \sum 22 PAHs is 0.04 to 167 mg kg⁻¹ with a mean of 2.2 mg kg⁻¹ and a median of 0.72 mg kg⁻¹ (Creaser et al., 2007). (The mean \sum 22 PAHs for UK urban soils is 25.7 mg kg⁻¹.) Clearly, the RHC contains considerably more PAHs than the average UK soil (and somewhat more than urban soil), but against this it has to be recognised that adding 10 t ha⁻¹ of RHC to soil only represents 0.25% of the soil mass to a depth of 23 cm. Hence, even a very large biochar addition of 60 t ha⁻¹ only represents 1.5% of the soil mass and the PAH concentrations in the RHC would be massively diluted (though could be concentrated on biochar particles in soil).

Guidance is available for assessing PAH addition to contaminated soils (Soil Screening Values), though this is unlikely to be appropriate for addition to agricultural soils. Nevertheless, applying the standard developed by the Environment Agency in England and Wales, the threshold for benzo(a)pyrene value is 0.15 mg kg⁻¹ (Merrington et al., 2008), while the one RHC sample

tested had a concentration of 0.08 mg kg⁻¹ (or 0.0008 mg kg⁻¹ in soil for a 40 t ha⁻¹ RHC addition). Meanwhile, urban soils in the UK contain a mean of 0.7 mg kg⁻¹ and rural soils 0.067 mg kg⁻¹ benzo(a)pyrene. The level of benzo(a)pyrene in the RHC is therefore relatively low. The Soil Screening Values provide a threshold also for toluene (0.3 mg kg⁻¹), whereas the value for BETX for two samples of RHC tested is higher at 7–22 mg kg⁻¹, though much lower (0.07–0.022 mg kg⁻¹) in soil with a 40 t ha⁻¹ RHC addition. The same guidance provides threshold values for several other chemicals, but notes that these SSVs are 'currently insufficiently reliable': naphthalene (0.0533 mg kg⁻¹, compare 10.4 mg kg⁻¹ in the RHC sample or 0.104 mg kg⁻¹ in soil (40 t ha⁻¹ RHC addition)), anthracene (0.02 mg kg⁻¹, compare 1.21 mg kg⁻¹ in the RHC sample (or 0.012 mg kg⁻¹ with 40 t ha⁻¹ RHC addition), and a mean value of 0.256 mg kg⁻¹ in English soils (Creaser et al., 2007)) and benzene (0.2 mg kg⁻¹) (Merrington et al., 2008). The problem with relying upon these numbers in assessing PAH levels in biochar is that they are developed for contaminated soil amendments and are not currently reliable.

The evaluation of PTOCs in biochar, and whether they may pose risks for soils and ecosystems, is highly uncertain at the current time; hence it is very difficult at present to define acceptable and safe levels of PAHs and other organic molecules in amendments to soil. The RHC contains fairly low levels of potentially dangerous PAHs, and the extraction method used in this study is fairly 'aggressive' because of the high sorption properties of the biochar and there is a major question concerning whether biochar will act to retain PAHs in soils. Beesley et al. (2010) found, for example, that bio-available PAHs were half of the 'totals' in contaminated soil, where biochar was used a soil amendment, probably due to sorption of PAHs into the biochar.

7. Potential contamination arising from the process

A sample of the sludge at the bottom of the settling pond was analysed and the results are shown in Table 4. The PAH level of the sludge sample is significantly greater than the total 16 PAHs in the

Table 4
Analysis of PAHs in rice husk char and in gasifier settling pond sludge and comparison with some measured soil levels and regulatory guidance on limits. For a 40 t ha⁻¹ RHC addition to soil, the values for PAHs in column 2 can be divided by 100 to allow direct comparison with the standards for soil contaminants presented in columns 4 and 5.

PAH (all in mg kg ⁻¹)	RHC sample	Settling pond sludge (mg kg ⁻¹ dry weight)	Eco-soil screening levels (USEPA) (mg kg ⁻¹ dry weight)	Contaminated soil reference (BG CLR17) (mg kg ⁻¹ dry weight) ^a	Maximum in product (mg kg ⁻¹ under Flemish law)
BETX		500–1000			
Total phenols		100–500			
USEPA \sum 16 PAHs	35	3223		629.9	
Naphthalene	10.41	1214	29–100	29.9	2.3
1-Methylnaphthalene	1.77	172	29–100		
2-Methylnaphthalene	1.36	152	29–100		
Acenaphthylene	4.59	733	29–100	26.8	
Acenaphthene	0.81	73	29–100	10.3	
Fluorene	0.38	114	29–100	42.8	
Phenanthrene	7.63	586	29–100	125.1	0.9
Anthracene	1.21	< 0.01	29–100	51.1	
Fluoranthene	3.73	93	29–100	102.1	2.3
Pyrene	2.19	75.8	1.1–18	85.8	
Benzo(a)anthracene	0.21	3.5	1.1–18	41.1	0.68
Chrysene	0.39	4.9	1.1–18	27.5	1.7
Benzo(b)fluoranthene	0.01	< 0.01	1.1–18	18.8	2.3
Benzo(k)fluoranthene	0.06	1.1	1.1–18	16.8	2.3
Benzo(a)pyrene	0.08	0.49	1.1–18 0.15 (UK EA)	28.4	1.1
Indeno(1,2,3-cd)pyrene	< 0.01	< 0.01	1.1–18	11.9	1.1
Dibenzo(a,h)anthracene	< 0.01	< 0.01	1.1–18	2.2	
Benzo(g,h,i)perylene	< 0.04	< 0.01	1.1–18	9.3	1.1

^a Graham et al. (2006), Table 3, p. 85, ASE method.

contaminated soil sample BG CLR17. Interestingly, the distribution between the 16 USEPA PAHs in the sludge sample varies considerably. There are relatively small quantities of the (generally more toxic) higher molecular weight (HMW) PAHs: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1.2.3-cd)pyrene and benzo(g,h,i)perylene for example; whereas, the contaminated soil sample contains far greater levels of these PAHs. It can be seen from Table 4 that the sludge sample has values of LMW and HMW PAHs, which far exceed the eco-SSLs for both invertebrates and mammals. For most PAHs, the levels in both the sludge sample and the RHC from the sludge are too high to permit application to soils using the Flanders' threshold values.

Given the high pollutant load of the black water and the settling pond sludge, it is clearly desirable for a clean-up system to be in place. The manufacturer Ankur Scientific has now designed a dry char discharge system using a screw auger and a black water filtration system using sand and activated carbon (Nagori, 2010). However, a clean-up system has not been observed in operation in Cambodia and there is no requirement or incentive for a gasification unit operator to install such a clean-up system. The environmental and health impacts of the black water and tarry residues from the gasifiers are not known. Enough is known about the risks of organic contaminants in soils, however (Creaser et al., 2007; Merrington et al., 2008), to recognise that there is a very real risk of harm. This is therefore a major weakness in the sustainability of the GBS, albeit it not related directly to the use of the RHC. I.e. the pollution problem arises from the operation of the gasifiers and would occur with or without use of the RHC. One sensible precaution is to use only RHC and not mixtures of RHC and sludge and/or other waste streams from the process.

8. Potential health issues

Another issue of potential concern is the health impacts arising from exposure to RHC. There are a range of possible concerns:

silicosis (chronic, accelerated or acute), scleroderma, lupus, arthritis, tuberculosis and kidney disorders (Bronzeoak, 2003) and cancer. The International Agency for Research on Cancer (IARC) undertook an exhaustive review of silica published in 1997 (IARC, 1997) and concluded the following:

“There is sufficient evidence in humans for the carcinogenicity of inhaled crystalline silica in the form of quartz or cristobalite from occupational sources. There is inadequate evidence in humans for the carcinogenicity of amorphous silica” (IARC, 1997, p. 210).

The UK Health and Safety Executive has likewise concluded the following:

“The weight of evidence from epidemiological studies, combined with evidence from animal studies and current understanding of the likely toxicological mechanisms underpinning the development of lung cancer in rats exposed to respirable crystalline silica (RCS), supports the view that RCS has the potential to cause lung cancer in humans” (Executive, 2003, p. 5).

“The balance of evidence suggests that heavy and prolonged occupational exposures to RCS can cause an increased risk of lung cancer. ... of the very many studies available, most of which clearly demonstrate excess mortality and morbidity from silicosis, there are few studies that, taken in isolation, provide reasonably convincing evidence for an increase in lung cancer that can be attributed to RCS. This appears to support the view that RCS is a relatively weak carcinogen, otherwise the evidence for lung cancer would be far clearer and convincing than is the case” (Executive, 2003, p. 5).

Crystalline silica is produced from amorphous silica at temperatures $> 800\text{ }^{\circ}\text{C}$, hence might be anticipated to form during gasification. In order to explore this, X-ray diffraction (XRD) studies were conducted of both rice husk char and rice husk

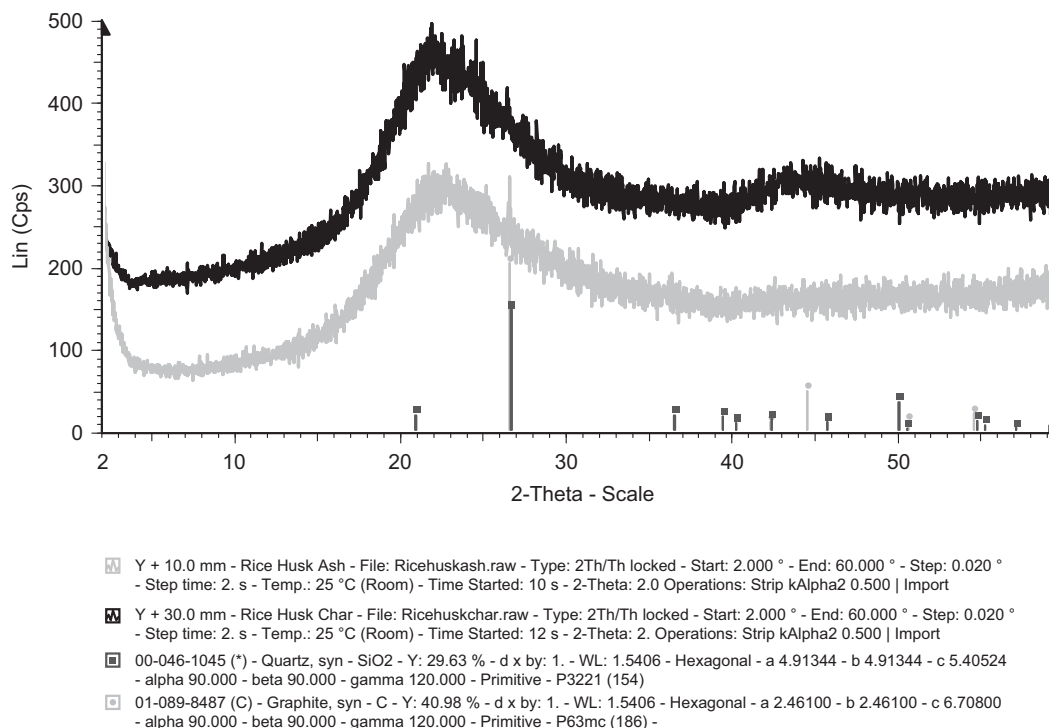


Fig. 6. X-ray diffraction (XRD) of carbonised rice husk (black line) and rice husk ash (grey line).

ash. The results are shown in Fig. 6. The black curve is the result for rice husk char while the grey curve is the result for rice husk ash produced by complete combustion of rice husks. The darker shaded vertical lines on the X-axis show the position for SiO₂ (quartz) and the lighter shaded line the position for graphite. The traces show a broad 'hump' centred on 22–23° 2-theta, which is non-specific. There is a peak at 26.5° in both traces, clearer in the ash trace. This, however, is the angle characteristic of both graphite and quartz. Further tests are therefore necessary to determine to what extent the silica is amorphous or crystalline or both. One option is to use a thermo-gravimetric analyser differential scanning calorimeter (TG-DSC).

Part II of the paper includes analysis of the field trials, carbon abatement and economics and pulls together all the information in an evaluation of the sustainability of the gasification–biochar system.

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