



# Source apportionment of carbon during gasification of coal–biomass blends using stable carbon isotope analysis



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## ABSTRACT

Stable carbon isotope analysis, a unique analytical technique, has been utilized for distinguishing and quantifying the individual contributions of coal and biomass feedstocks in the generation of carbon containing gases during the gasification of their blends. For this purpose, corn stover (CS) and switchgrass (SG) were individually blended up to 30% by weight with two different Montana coals, namely, DECS-38 sub-bituminous coal (SB) and DECS-25 lignite coal (LG) and gasified at atmospheric pressure with varying O<sub>2</sub>/steam ratios. Gasifying at a constant O<sub>2</sub>/steam ratio while increasing percentage of biomass in the feedstock resulted in an increase of  $\delta^{13}\text{C}$  (‰) values for the carbon containing product gases. An increase in the concentration of oxygen in the feed stream at a constant biomass percentage leads to the depletion of <sup>13</sup>CO and enrichment of <sup>13</sup>CO<sub>2</sub> in the blends with corn stover while an enrichment of both <sup>13</sup>CO and <sup>13</sup>CO<sub>2</sub> was observed in blends with switchgrass. Based on isotope mass balance considerations, the contribution of corn stover was in the range of 1% – 40% for CO generation and 6% – 69% for CO<sub>2</sub> generation. Switchgrass, on the other hand, contributed up to 53% for CO generation and only 46% for CO<sub>2</sub> generation.

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## 1. Introduction

The past few years have seen an upsurge in interest in the gasification of biomass and coal–biomass blends for several reasons. They include [1]:

1. Reduction in greenhouse gas emissions caused by the combustion of fossil fuels.
2. A need for energy independence due to the depleting resources and fluctuating prices of oil and natural gas.
3. Developing interest in renewable energy resources.

Although there is an abundance of coal in the United States and several other countries and it will continue to be a major source of energy for many years to come, there is still great interest in replacing part of the coal used in energy generation with renewable biomass or plant-derived organic matter available on a renewable

basis [2]. Many countries have initiated incentives in recent years to encourage the co-utilization of biomass and coal for energy production [3]. Biomass fuels (BF) are to be sustainable natural resources if they renew themselves at such a rate that they will be available for future use. That is, if the rate of consumption of BF is  $\leq$  the rate at which it is generated. These BF resources can be either grown and harvested biomass such as switchgrass or waste biomass such as corn stover, wood wastes from forestry and lumbering operations, wastes from paper production, and landscaping wastes [2].

There are various techniques available for coal gasification. Considering the huge amount of greenhouse gases generated during the process of gasification, new methods are being developed [4]. The idea of gasifying mixtures of coal and biomass is relatively new with almost zero commercial experience since the properties of coal and biomass differ significantly from each other [5–8]. Co-processing these feedstocks, with oxygen and steam in relevant proportions with respect to the amount of carbon results in the formation of mainly CO, CO<sub>2</sub>, H<sub>2</sub> and small quantities of lower hydrocarbons. Prins et al. [9] reported that fuels with higher oxygen to carbon ratios have larger energy losses due to their high ratio of available chemical energy to heating value. Such fuels are over-oxidized (combusted) in the gasifier to attain the required

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gasification temperature. Therefore, highly oxygenated fuels are not ideal for gasifiers keeping in view the energy losses that can be incurred and hence, solid biomass can be more readily gasified if it is co-gasified with coal [3]. Hence, co-gasification of blends of coal and biomass to produce syngas (CO–H<sub>2</sub> mixtures) is an open area for future research. The CO<sub>2</sub> generated during the combustion of BF is neutralized by the utilization of atmospheric CO<sub>2</sub> through photosynthesis during biomass growth. Therefore, it is imperative to quantify the contribution of these biomass feedstocks in the generation of greenhouse gases. Stable carbon isotope analysis is one such technique that can be utilized to know the source of gases generated during co-processing [10–13].

## 2. Theory

Stable carbon isotope composition is determined as the ratio of <sup>13</sup>C/<sup>12</sup>C in a substance relative to Pee Dee Belemnite (PDB), a cretaceous marine fossil having an anomalously high <sup>13</sup>C/<sup>12</sup>C ratio, which is an internationally established reference standard for the stable isotope composition of carbon in natural materials. Carbon isotope ratios are commonly reported using delta notation (as δ<sup>13</sup>C values) in parts per thousand (per mil, ‰) [10,11,14–21] as shown in Eq. (1).

$$\delta^{13}\text{C} = \left( \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} - 1 \right) \times 1000\text{‰} \quad (1)$$

Most plants can be divided into three groups based on the photosynthetic pathway by which they fix carbon [22–24]:

1. C<sub>3</sub>: Almost 95% of the plants on earth fall under this category. They fix carbon dioxide by the Calvin cycle and have δ<sup>13</sup>C values that generally range between –23 and –34‰. Examples of these plants include temperate shrubs and trees and grasses.
2. C<sub>4</sub>: These plants fix carbon dioxide by the Hatch–Slack cycle. Their δ<sup>13</sup>C values are less negative and range between –8 and –16‰. Plants like corn, switchgrass and warm weather grasses, predominantly, belong to this category.
3. CAM: The third group of plants fixes carbon dioxide by the Crassulacean Acid Metabolism pathway, and have δ<sup>13</sup>C values that are intermediary compared with C<sub>3</sub> and C<sub>4</sub> plants.

Fossil fuels such as coal and oil are made primarily of C<sub>3</sub> plant material and are depleted in <sup>13</sup>C relative to the atmosphere, because they were originally formed from living organisms [21,25]. Therefore, the carbon from fossil fuels that is returned to the atmosphere through combustion is depleted in <sup>13</sup>C when compared to atmospheric carbon dioxide. The values of δ<sup>13</sup>C vary by measurable amounts for different carbonaceous materials depending on their carbon source, fixation pathway, environment of formation and post depositional history. These values differ by about 10–15‰ for coal and biomass materials with the δ<sup>13</sup>C for coal being more negative than that of biomass. This means that the carbon contained in coal is richer in <sup>12</sup>C, as is the case with all fossil fuels. Surprisingly, the carbon isotope composition of coal typically does not vary much with increasing coal rank which implies that significant fractionation does not occur during its decomposition [21,25,26].

Most of the previous works involving coal co-processing that utilizes isotope mass spectrometry are related to the sourcing of coal–bitumen or coal–oil co-processing or gasification of carbon composite materials [14–17,26,27]. Steer et al. [17] studied the efficacy of Highvale coal and Suncor bitumen co-processing using this technique and provided a valid isotope mass balance method to quantify the amount of coal incorporated in each distillate fraction of their liquefaction process [17]. The synthetic oil generated from their process had intermediate isotope ratios which were directly proportional to the amount of coal

incorporated in the feedstock. Lancet et al. [15,16] and Winschel et al. [27] determined the individual contributions of various coal/petroleum feedstocks under varied conditions and demonstrated that stable carbon isotope analysis can be a quantitative tool to independently assess the relative reactions of carbonaceous feedstocks during co-processing [15,16,27]. In these studies, the isotope ratios of product gas samples were not obtained directly; instead, a forced carbon balance was utilized to obtain information on the gas products. These studies concluded that during actual co-processing, considerable bond breaking occurs. Because <sup>13</sup>C–<sup>12</sup>C bonds are slightly stronger than <sup>12</sup>C–<sup>12</sup>C, heavier organic residues like tar and vacuum bottoms were presumed to be enriched in <sup>13</sup>C while lighter hydrocarbon gas products were enriched in <sup>12</sup>C relative to the feed. Therefore, the isotope ratios in such cases would never be intermediate to the parent sources. Further complications may arise if isotope ratios in product materials change over time depending on the extent of the reactions. For cases in which the generation of light hydrocarbons such as methane is very low and when isotopic mass balances are not affected in a huge way, the isotope analysis would still be very useful for envisaging product trends that occur during co-processing. Thomas et al. [26] performed isotope ratio mass spectrometry to study the gasification of carbon composites manufactured from the co-processing of coal tar pitch fibers and petroleum pitch matrix. They observed that heat treating the composite produced changes in the carbon isotope composition of the reactant which may be due to different δ<sup>13</sup>C values for the product gas and solid phases. Partially gasifying the carbon composites lowered their δ<sup>13</sup>C values by about 4‰ due to the loss of <sup>12</sup>C enriched gases such as methane and that the δ<sup>13</sup>C values for the composites change as function of gasification temperature. Also, the products had intermediate δ<sup>13</sup>C values compared with the parent materials and hence, reactions occurring during co-processing were easily distinguishable [26].

This paper describes the utilization of stable carbon isotope analysis for distinguishing and quantifying the individual contributions of coal and biomass feedstocks towards the generation of carbonaceous product gases, in particular, CO and CO<sub>2</sub>. Although this application has been available for many years and used mostly in bio-geo-chemical studies, very limited information is available in literature with regards to this particular analysis for blends of coal and biomass. Experimental data obtained by this method can provide valuable information for analyzing the interactions and synergy between the feedstocks and also for process modeling and optimization of production methods.

## 3. Experimental

### 3.1. Materials

For the purpose of this work, two different biomass samples, namely, corn stover (CS) and switchgrass (SG) were blended individually up to 30% by weight with two different ranks of non-composite Montana coals, namely, DECS-38 sub-bituminous coal (SB) and DECS-25 lignite coal (LG) [28]. The US Department of Energy Coal Samples (DECS) used in this work were obtained from the Pennsylvania State University Coal Sample Database while the biomass samples were provided by the Center for Applied Energy Research at the University of Kentucky. The DECS-38 sub-bituminous coal was collected from Dietz seam of Bighorn County while the DECS-25 lignite coal was collected from Pust seam of Richland County located in Montana, USA [28]. Detailed information regarding coal sample history, sampling information from the coal field, maceral composition and reflectance data is available through the Pennsylvania State University Coal Sample Database [28].

The proximate and elemental analyses of all the feedstock samples are listed in Table 1. Proximate analysis of the feedstock samples was conducted according to ASTM standard D7582-12 [29] using a Netzsch Jupiter STA 449 Simultaneous Thermal Analyzer. The percentages of C, H, and N in the feedstock samples were determined

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