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ORIGINAL RESEARCH

The effect of oxygen on formation of syngas contaminants during the thermochemical conversion of biomass

Dennis Schuetzle[1] · Robert Schuetzle[2] · S. Kent Hoekman[3] · Barbara Zielinska[3]

Abstract The effect of oxygen on the formation of syngas contaminants during the thermochemical conversion of carbonaceous feedstocks has been quantified using an integrated biorefinery plant operated at a biomass input of about 4.5 metric tons/day. This plant combines solids steam reforming and gases steam reforming processes for the conversion of biomass to syngas. It was found that the presence of low concentrations of oxygen (in air) during the thermochemical conversion process had a significant effect on the formation of contaminants in the syngas. For example, particulate organic carbon compounds (organic particulate contaminants) increased from 3.3 to 122 mg/m^3 when the oxygen input was increased from 225 ppm to 4.1 vol.% during the thermochemical conversion of wood to syngas. It is proposed that the primary free radical (*) species H*, OH*, O*, CH$_3$* and OOH*, formed from the presence of O$_2$ in this high-temperature process, react with the myriad of organic compounds in the syngas at varying rates, depending upon their structure and reactivity. These processes represent the primary chemical mechanisms for the formation of high molecular weight hydrocarbons, polynuclear aromatic hydrocarbons, oxygenated hydrocarbons and polymeric materials, commonly referred to as organic particulate contaminants. The potential importance of these free-radical oxidation processes was supported by measuring the concentrations of selected oxygenated hydrocarbons in the syngas over a range of 225 ppm to 4.1 vol.% of O$_2$ in the thermochemical process. The concentrations of oxygenated polycyclic aromatic hydrocarbons (hydroxy-naphthalene, dihydroxy-naphthalene, dihydro-indene-2-one, and benzo-pyranone) increased by 732, 244, 83 and 195 times, respectively, when the oxygen concentration was increased from 225 ppm to 2.5 vol.%. These increases were due to the free-radical oxidation of the highly reactive PAHs during the thermochemical processes. The importance of these oxidation processes was further confirmed by studying the decrease of easily oxidized olefins. For example, the concentrations of 1,3-butadiene, acetylene, propene and ethene decreased by 9.3, 5.2, 4.5 and 3.4 times, respectively, when oxygen in the plant was increased from 1.6 to 2.5 vol.%. It is concluded that the formation of organic particulate contaminants during the thermochemical conversion of carbonaceous feedstocks can be minimized by maintaining the concentration of oxygen below 500 ppm.

✉ Dennis Schuetzle
dennis@reii.us

1 Renewable Energy Institute International (REII), 2020 L Street, Sacramento, CA 95811, USA

2 Greyrock Energy, 2020 L Street, Sacramento, CA 95811, USA

3 Division of Atmospheric Sciences, Desert Research Institute (DRI), 2215 Raggio Parkway, Reno, NV 89512, USA

Introduction

For reasons of energy security, diversity, and climate change concerns, there is growing interest in utilizing lignocellulosic materials as feedstocks for fuels and

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chemicals. DOE's Office of the Biomass Program has established a comprehensive *Biomass Multi-Year Program Plan*, which defines goals and strategies for the use of biomass resources in helping address the US's energy challenges [1].

Various thermochemical, biochemical and physico-chemical conversion processes have been developed for the conversion of biomass and other renewable feedstocks to fuels and chemicals. These processes are typically referred to as integrated biorefineries (IBR), in which biomass is converted into fuels and chemicals [2, 3]. The potential of these processes is supported by DOE's recent studies demonstrating that up to one billion tons of biomass per year are available in the US for the production of fuels and chemicals [4, 5].

Thermochemical conversion (or gasification) is a very versatile process that utilizes varying concentrations of heat, steam and oxygen to convert nearly any solid, liquid or gaseous carbonaceous feedstocks to syngas. This syngas consists primarily of H_2 and CO with minor concentrations of CO_2 and CH_4. In addition, tars and other syngas contaminants are formed which must be removed before the syngas can be used to produce fuels and chemicals.

Thermochemical conversion technologies have certain advantages and disadvantages over biochemical conversion technologies [6]. The main advantages are that the feedstock for thermochemical conversion can be any type of biomass including agricultural residues, forestry residues, non-fermentable byproducts from biorefineries, byproducts of food industry, byproducts of any bioprocessing facility and even organic municipal wastes; and the product gases can be converted to a variety of fuels (diesels, synthetic gasoline) and chemicals (methanol, ethanol, urea) as substitutes for petroleum-based chemicals. A major disadvantage of thermochemical conversion is the high costs associated with cleaning the product gas from undesirable contaminants.

In contrast, biochemical processes are feedstock selective and the range of products that can be produced from a particular feedstock is limited. Biological routes to fuels using lignocellulosic feedstocks, such as hydrolysis and fermentation to ethanol, involve pre-treatment steps and subsequent biological processes that are optimized for particular biomass types. As a result, many of these routes have a limited ability to accept mixed or variable feedstocks such as wastes.

There are a multitude of thermochemical conversion process designs which can be classified in terms of the direction of the biomass flow and the method of heating [7]. These processes typically utilize indirect, direct and hybrid reactor designs as follows:

1. *Indirect* The carbonaceous materials are input into relatively large vessels that are heated externally in the absence of oxygen or air. Steam is typically added to facilitate the conversion of the carbonaceous materials into syngas. These processes are typically operated at less than 1800 F (982 °C) and with relatively long residence times.

2. *Direct* This process requires the addition of an oxidant (oxygen or air) with the biomass in order to internally generate the required thermal energy for efficient conversion to syngas.

3. *Hybrid* Several commercial systems perform the primary thermochemical conversion using indirect heat and a relatively small amount of an oxidant (oxygen or air). The solid carbon residues are then passed to a second vessel in which they are partially oxidized to increase the production of syngas.

All of these thermochemical conversion processes produce various levels of gas-phase and particulate-phase syngas contaminants [8–10], depending upon their design and operating conditions. These particulate-phase contaminants are commonly referred to as organic particulate contaminants, which consist primarily of polynuclear aromatic compounds, high molecular weight hydrocarbons, oxygenated hydrocarbons and polymeric materials. Previous studies have demonstrated that the composition and quantity of these organic particulate contaminants are influenced by thermochemical system operating conditions. For example, it has been found that organic particulate contaminants are reduced by about a factor of five by increasing thermochemical operating temperatures from 750 to 950 °C [11]. However, no studies have been reported to date that quantify the effect of oxygen on the concentrations of organic particulate contaminants in syngas during thermochemical conversion processes. Therefore, the primary objective of this study was to determine the effect of oxygen on the formation of gas-phase and particulate-phase contaminants during the thermochemical conversion of wood to syngas.

These organic particulate contaminants can have significant adverse effects on downstream catalysts that are used in processes that convert syngas to fuels [12]. Therefore, rigorous syngas quality specifications have been established by several organizations to help insure long catalyst life. For example, the syngas quality specifications established by Greyrock Energy for the production of 'drop-in' diesel fuel are summarized in Table 1 [13]. In addition, several groups have established $\sim$5 mg/m^3 limits for organic particulate contaminants (tars) in syngas used in direct-fired, industrial gas turbines, and 10–50 mg/m^3 for syngas used in spark ignition and diesel engines [8].

Table 1 Maximum recommended contaminant levels for the catalytic conversion of syngas to "drop-in" diesel fuel [11]

Catalyst contaminants	Maximum recommended contaminant levels
Hydrogen sulfide (H_2S) and carbonyl sulfide (COS)	<20 ppb
Sulfur dioxide (SO_2)	<20 ppb
Oxygen (O_2)	<500 ppm
Ammonia (NH_3)	<75 ppb
Hydrogen chloride (HCl)	<35 ppb
Nitric acid (HNO_3)	<50 ppb
Total organic and inorganic particulate matter (PM)	<500 $\mu g/m^3$

Objectives

The thermochemical process developed, deployed and tested in this study utilizes indirect heating (Fig. 1). This process was selected since preliminary studies carried out by our group during 2005–2007 [14] demonstrated that this approach had the greatest potential of:

1. Significantly reducing the production of gas-phase and particulate-phase contaminants in the syngas, resulting in reduced capital, operating and maintenance costs required for syngas purification.
2. Maximizing the concentrations of CO and H_2 and minimizing the concentrations of CH_4 and CO_2 in the syngas, resulting in an increased production of fuels and chemicals.
3. Directly producing H_2 and CO with H_2/CO ratios in the optimum 2.00–2.30 range required for the production of fuels and chemicals, which eliminates the need for additional unit process such as reverse water gas-shift reactors, hydrogen generators, pressure swing absorption systems, etc.

4. Producing high-purity syngas in which oxygen and other gas-phase and particulate-phase contaminants are at very low levels so that the catalysts used for the direct production of liquid fuels will not be adversely affected.

Therefore, the work described in this paper focused on quantifying the potential effect of oxygen on the production of gas-phase and particulate-phase contaminants and on the concentration of H_2 and CO in the syngas.

Experimental

A pilot-scale integrated biorefinery (Fig. 1) was employed for this investigation. Figure 1 illustrates the primary unit operations used for the conversion of biomass to fuels. The thermochemical conversion (TCC) process includes unit operations #1–#4 in which the biomass is converted to purified syngas. The production of "drop-in" fuels from the syngas includes unit operations #5–#8. This paper is focused on the potential effect of O_2 on the production of

Fig. 1 Process flow diagram for the pilot plant
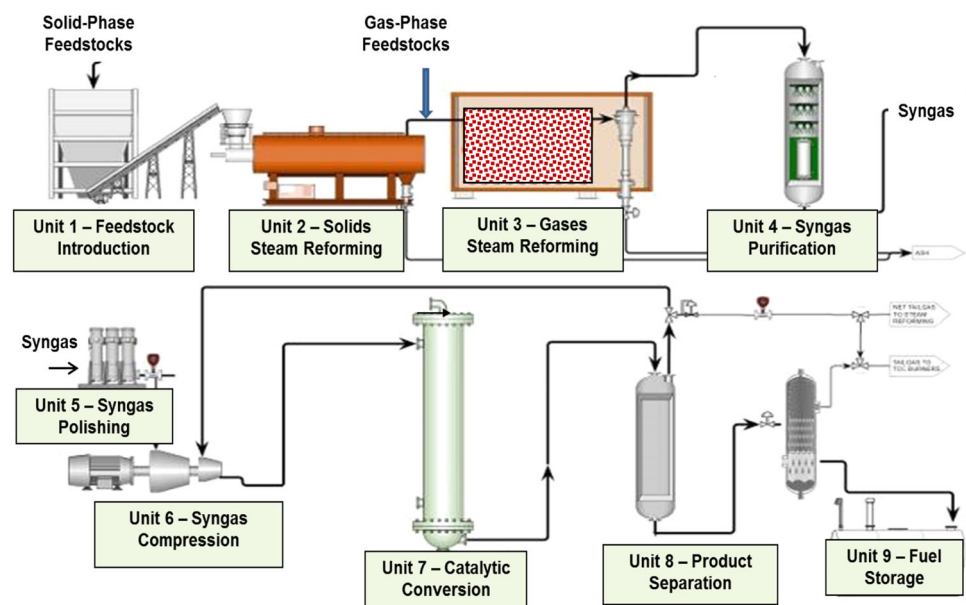
organic particulate contaminants in unit operations #1–#4. This integrated biorefinery was operated at about 4.5 metric tons/day biomass input.

Integrated biorefinery

The pilot integrated biorefinery (Fig. 1) utilizes a two-step steam reforming process that employs heat, pressure and steam in the absence of O_2, coupled with a gas purification system, to produce a clean syngas, intended for subsequent catalytic conversion to high-quality, synthetic diesel fuel [13]. The TCC process comprised four primary unit operations: #1—feedstock introduction, #2—solids steam reforming, #3—gases steam reforming, and #4—syngas purification.

In unit operation #1, the feedstock is flushed with carbon dioxide to remove any entrained air before it is fed into the solids steam reforming unit operation #2. An oxygen sensor is used to monitor any remaining oxygen, which was found to average 225 ± 30 ppm during the several days of plant operation.

Unit operation #2 utilizes a specifically designed retort chamber that operates in the 1400–1550 F (760–843 °C) range. The retort is a long cylinder with a series of internal spiral flights. The retort was manufactured from a wrought alloy, RA-330, that is suitable for the temperature range (i.e., 1700 F (927 °C) maximum) and not reactive with the pyrolysis compounds. The outer casing was designed to withstand 345 kilopascals (50 psig) internal pressure. The vessel and dished ends were constructed of mild steel plates per American Society of Mechanical Engineers (ASME) boiler pressure vessel codes. Ceramic fiber modules, 25 cm thick and 10 in. thick with a density of 160 kg/m^3, were provided and stud welded to the furnace sidewalls, roof, and discharge end wall. The retort rotates around its longitudinal axis such that the spiral flights convey the feedstock from end to end in a defined period of time. Various devices (e.g., bars and rakes) are used between the flights to cause the feedstock to tumble and improve the rate of heat transfer.

The heating system consists of 36 single-ended radiant (SER) tubes and burners arranged along the sides of the retort that is divided into three equal and independent zones of temperature control. Zone control is implemented in the process control programmable logic controller (PLC). Infrared temperature sensors are provided in each zone to monitor and record the retort temperature profile.

Natural gas is used to fire the SER burners during startup operations, but once steady-state conditions have been achieved, tailgas (a methane-enriched syngas) from the liquid fuels production process may be substituted.

Ash is removed at the end of the retort with an integrated water-cooled auger system. The ash is depressurized to ambient conditions through a valve-lock/hopper system. The solid particles are composed primarily of unconverted carbon, silica, metal oxides, and trace minerals. The ash has commercial applications including as a soil enhancer and in ceramics manufacturing.

A pressure transmitter is provided to monitor and record the pressure inside the solids steam reforming chamber. Control of this pressure is affected by downstream equipment. For example, the chamber pressure will rise if the discharge flow is reduced. Likewise, the pressure will decline if the discharge flow is drawn away faster than the feedstock is supplied. A pressure relief device is provided in the event of a high-pressure control malfunction in downstream equipment.

Unit operation #2 is a slow pyrolysis process that utilizes a purge gas (steam or carbon dioxide) to convert the solid-phase carbon to gas-phase carbon species in the absence of oxygen ($O_2 < 500$ ppm). The residence time of the feedstock can be varied from about 5–20 min by changing the rotation speed of the retort.

During this solids steam reforming process, it was found that the carbon in the feedstock was efficiently converted to gas-phase organics and syngas using a steam to feedstock carbon mass ratio of about 1.4/1.0. This ratio is controlled to maximize the conversion of solid-phase carbonaceous compounds into gas-phase carbonaceous products. The average feedstock carbon to syngas carbon conversion efficiency for wood was found to average 85 weight% under the operating conditions [13] summarized below.

Unit operation #3 was designed to steam reform the gas-phase products, generated from unit operation #2, into syngas. This unit operates at a tube temperature of 1790–1815 F (977–991 °C), at a pressure of up to 345 kilopascals (50 psig) and with gas residence times of 3–8 s. The steam injected into unit operation #3 is superheated with the exhaust from the solids steam reforming chamber burners. The heat exchanger is constructed from an iron/nickel/chromium-based alloy selected for its high-temperature tensile strength, longevity and low maintenance. The steam-to-carbon mass ratio is maintained at about 1.4/1.0. The gas-phase products from the solids steam reforming process and superheated steam (unit operation #2) are injected into unit #3 for conversion of the gas-phase organic species into syngas. The resulting syngas is composed primarily of hydrogen (H_2) and CO, along with lower concentrations of methane (CH_4) and CO_2.

As shown in Fig. 2, unit operation #4 utilizes several processes to purify the syngas from unit operation #3 including the following: (#4-1) a cyclone to remove particles greater than about 3 μm in size; (#4-2); a quench column to collect organic particulate contaminants; (#4-3) a high-efficiency venturi water scrubber that cools the syngas and then removes organic particulate contaminants
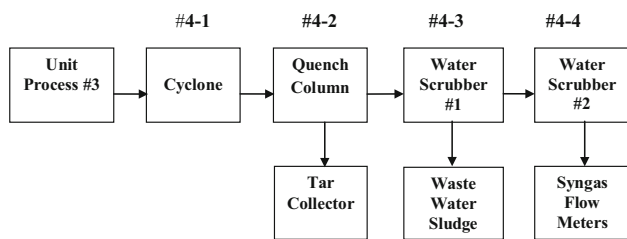
Fig. 2 Syngas purification sub-unit operations

and other fine particulates; (#4-4) a packed-bed scrubber tower and chemical scavengers to remove sulfur compounds (e.g., H_2S), ammonia, and oxygenated hydrocarbons. The organic particulate contaminants generated from the IBR plant are classified into two types:

1. *Type A Organic particulate contaminants* Aromatic compounds with 2–3 rings such as naphthalene and anthracene; oxy-arenes such as dihydroxy-benzene; and non-volatile hydrocarbons and oxygenated hydrocarbons such as hydroxy-undecane.
2. *Type B Organic particulate contaminants* Polynuclear aromatic hydrocarbons (PAH) with four or more rings (non-volatile organic particulate contaminants) such as pyrene and benzo (a) pyrene; oxy-PAHs such as hydroxy-naphthalene; and polymeric materials.

The oxygenated, volatile organic compounds, such as guaiacol and phenol, are removed easily in the water scrubber. Although the gas-phase aromatics, benzene and toluene, are not removed in the scrubber, it has been demonstrated that they pass through the catalyst bed unreacted without any adverse effect on the fuel production catalyst. Therefore, these volatile organics were not classified as organic particulate contaminants, even though they are typically included in the definition of "tars".

The cyclones (Fig. 2, #4-1) are installed inside the reforming chamber (unit operation #3) and operate at the elevated temperature of the chamber. This location limits the potential for condensation of unconverted higher molecular weight gaseous components inside the cyclones which would cause fouling and plugging problems and also preserves the thermal energy in the syngas for heat recovery opportunities. Ash is collected from the cyclones and cooled via a water-jacketed auger and valve-lock system.

Following the cyclones, the hot syngas is routed through a quench venturi scrubber system to cool and scrub any remaining particulates, condensable organic particulate contaminants, gases, and other contaminants. First, hot syngas from the cyclones is passed through a series of water-spray quench vessels, which cool the syngas and coagulate and remove the bulk of micro-particles and contaminants. The cooled syngas then passes through a

venturi scrubber to remove particles down to 0.5–1 μm in size. The syngas is next routed through an optional air cooler and then into a vertical packed-bed tower scrubber system.

The first quench spool is constructed of Hastelloy™ to handle the high-temperature incoming syngas. All following vessels, lines, the venturi, and packed bed are constructed of 316 stainless steel.

The vertical packed scrubber tower is used to scrub the syngas of sulfur species (such as SO_2, H_2S) using solutions of sodium hydroxide and hydrogen peroxide. The scrubber water pH is maintained at 9–10 to maximize scrubber efficiency [13]. Particulate matter is removed from the scrubbing water after passing through a press filter and chiller.

The plant was run at a constant feed rate of about 4.5 metric tons/day using wood chips. The composition of these chips is summarized in the next section. Once it was demonstrated that the plant was operating under stable, steady-state conditions, the following operating data were collected:

1. Biomass feed rate (metric tons/h)
2. Temperatures at various locations in the thermochemical system
3. Steam-to-biomass feed ratios
4. Volume of syngas produced per minute (cubic meters/ min).

Experimental

Biomass feedstock

The wood chips used in this study ranged from 0.15 to 2.5 in. (0.40–6.4 cm) in size. They were sourced from the Michigan and Ohio area and consisted of about 85 % hardwoods and 15 % softwoods. Wood chips, less than about 0.40 cm., were removed by screen segregation. Table 2 summarizes the elemental composition of the wood chips. This concentration of elemental species is typical of that for Midwest hardwood samples.

The moisture content of the feedstocks was used to determine how much steam should be fed into the pilot plant as well as for determining the feedstock carbon conversion efficiency to fuel. Feedstock moisture analysis was carried out using a drying oven following ASTM method #D442. The moisture content of the wood chips averaged 14.0 weight% during these tests.

Table 2 also summarizes the average volatile organic carbon and fixed (elemental) carbon constituents in the total feedstock carbon content. It was determined that 86.2 and 13.8 weight% of the 50.0 % of carbon in the wood

Table 2 Chemical composition and energy content of the wood feedstock

Chemical species	Wt.% (dry basis)
Carbon	50.0
Hydrogen	5.97
Oxygen	42.3
Nitrogen	0.23
Sulfur	0.01
Chlorine	0.001
Calcium	0.20
Potassium	0.11
Aluminum	0.003
Magnesium	0.02
Iron	0.007
Sodium	0.02
Carbon analysis	Wt.% (dry basis)
Volatile organic carbon	86.2
Fixed carbon (elemental)	13.8
Energy content	MJ/kg (dry basis)
Lower heating value (LHV)	17.57
Higher heating value (HHV)	20.48

feedstock was volatile organic carbon and fixed (elemental) carbon, respectively.

Oxygen input

Various levels of air were input to the pilot plant to increase the O_2 concentration in five increments from 225 ppm to 4.1 vol.% to determine the effect of O_2 on the concentration of gas-phase and particulate-phase contaminants in the syngas. The concentration of N_2 in the syngas was used to estimate the average concentration of O_2 that was input into the process, as air. O_2 concentrations were also measured in real-time using a Teledyne Model 3190 Oxygen Analyzer. The accuracy of these measurements was about ± 5 %. We define an O_2-free environment when the O_2 is less than about 500 ppm.

Real-time syngas analysis

The concentrations of the major syngas constituents were monitored using a gas analysis system permanently installed at the pilot plant. Integrated syngas samples were collected in Tedlar bags and the major constituents (H_2, CO, CO_2, CH_4 and N_2) were determined using gas chromatography (GC). On-line measurements of H_2, CO, CO_2 and CH_4 were also made using a Siemens Maxum Edition II Process GC. Syngas samples were also collected and

Table 3 Measured syngas composition and calculated O_2 input from the pilot IBR plant utilizing wood feedstock

Oxygen input	Syngas composition (vol.%)[a]					
	N_2	H_2	CO	CH_4	CO_2	H_2/CO
225 ppm	<0.20	49	23	12	17	2.1
1.0 vol.%	3.7	44	22	13	16	2.0
1.6 vol.%	5.9	44	22	13	16	2.0
2.5 vol.%	9.2	43	19	11	20	2.3
4.1 vol.%	15.3	37	17	9	23	2.2

[a] Measurement accuracy for syngas constituents: ± 5 %

selected for comprehensive analysis during the test period. Table 3 summarizes the average levels of N_2, H_2, CO, CH_4 and CO_2 (± 5 % accuracy) measured in the dry syngas for the five sampling periods.

The volume% of N_2 measured in the syngas was used to estimate the volume% of O_2 input into the system as follows:

$$\text{Input } [O_2] = [N_2]/3.73$$

Since the pressure in the plant was kept constant throughout the process and since the syngas replaced the steam in the thermochemical process, the concentration of N_2 in the syngas was found to be approximately proportional to the concentration of O_2 input in the thermochemical conversion system.

Integrated syngas sampling

Syngas samples were collected once the plant was operating at stable, steady-state conditions. All syngas samples were collected before the final syngas cleanup (purification step). A dilution sampling and analysis approach recently developed and validated by DRI and REII was used to characterize trace contaminants in the syngas produced from thermochemical conversion of wood from the plant [15, 16]. This dynamic dilution sampling system was employed to minimize the potential loss of polar organic and particulate species during the sampling of the hot syngas. The hot syngas samples were collected after the cyclones and before the quench column (Fig. 2). Sample collection media included a combination of filters, adsorbent cartridges and evacuated canisters. Results were generated for up to 165 syngas contaminants generated from the conversion of the wood chip feedstocks over the test period.

Characterization of integrated samples

Special emphasis was placed on the characterization of trace sulfur compounds (H_2S and SO_2); nitrogen compounds (NH_3, HNO_3 and NO_2); chloride compounds (HCl

Table 4 Effect of oxygen on the concentration of particulate components in syngas generated from the thermochemical conversion of wood

Oxygen input	Syngas contaminants (mg/m^3)[a]		
	Particulate organic carbon	Particulate elemental carbon	Total carbon containing particulates
225 ppm	3.3	0.6	3.9
1.0 vol.%	6.4	4.1	10.5
1.6 vol.%	57	10	67
2.5 vol.%	194	75	269
4.1 vol.%	122	98	220

[a] Measurement accuracy for particulate organic carbon and particulate elemental carbon: ± 10 % above 2 mg/m^3 and ± 15 % between 0.05 and 0.50 mg/m^3

and inorganic chlorides); organic particulate contaminants (organic particulates); and inorganic particulate matter (elemental species) since these materials are known contaminants that can adversely affect catalysts used for conversion of syngas to fuels. Trace gas and particulate-phase organic and inorganic chemical species were collected from the syngas stream and characterized using the following procedures as described previously [14–16].

- Thermal optical analysis of total organic C (organic particulate contaminants) and total elemental C on quartz filters
- GC/MS analysis of C_1–C_{11} gas-phase volatile organic compounds (VOCs) and chlorinated VOCs (>50) in Summa stainless steel sampling canisters
- Ion chromatography (IC) of chlorides, nitrates and sulfates on quartz filters
- IC analysis of HCl, HNO_3 and SO_2 on K_2CO_3 impregnated cellulose filters
- GC/TCD and GC/FID analysis of major syngas constituents (6 species)
- GC/MS analysis of higher MW VOCs (C_8–C_{20}) (>25 species) collected on Tenax cartridges
- HPLC analysis of DNPH derivatives of C_1–C_7 carbonyl compounds (14 species)
- Colorimetric analysis of ammonia from citric acid impregnated cellulose filters
- X-ray fluorescence (XRF) analysis of $AgNO_3$-impregnated filters for measurement of H_2S (as AgS)
- XRF analysis of teflon filters for measurement of elemental constituents (51 species)

Gas samples were collected using Tedlar bags and electro-polished stainless steel canisters. Gas chromatography using thermal conductivity, sulfur-selective and nitrogen-selective detectors were used to measure O_2, N_2 and sulfur species in the syngas samples.

In this study, organic particulate contaminants are defined as the concentration of total organic carbon in the particulates collected on quartz filters at room temperature. The concentrations of specific organic particulate contaminants were determined from GC/MS analysis of C_8–C_{20} hydrocarbons collected from the Tenax cartridges and quartz filters. The possibility of break-through of gas-phase species during the Tenax sampling was assessed. It was found that the break-through was not a problem since the concentrations of gas-phase species were low.

Results

Table 3 summarizes the concentrations of the primary syngas constituents. The concentrations of H_2 and CO decreased as the concentration of O_2 increased while the ratio of H_2/CO remained relatively constant (2.15 $\pm$ 0.15). In contrast, the concentrations of CO_2 increased at oxygen inputs of 2.5 and 4.1 %.

Table 4 shows that the concentration of particulate organic carbon increased considerably from 3.3 to 122 mg/m^3 when O_2 in the system was increased from 225 ppm to 4.1 % during the thermochemical conversion process (the accuracy of these measurements are ± 15 % between 0.06 and 0.50 mg/m^3 and ± 10 % above 2 mg/m^3). This is not surprising since it is well known that organic compounds react readily with O_2 under high-temperature conditions to form oxygenated hydrocarbons and polymeric materials that have much lower vapor pressures than their respective hydrocarbon reactants [17–26]. Particulate elemental carbon also increased significantly from 0.6 to 98 mg/m^3 as O_2 was increased from 225 ppm to 4.1 %.

Table 5 summarizes the effect of O_2 concentration on particulate sulfates, nitrates, SO_2 and HNO_3 in the syngas. The concentrations of particulate sulfates were low (1.4 $\mu g/m^3$) when the O_2 concentration was 225 ppm but increased to 201 $\mu g/m^3$ when O_2 increased to 4.1 %. The concentration of SO_2 also increased from 1.8 to 240 $\mu g/m^3$ over this range of O_2 concentrations. These increases were probably due to the oxidation of reduced sulfur species (e.g., H_2S, COS, mercaptans and thiols) to gas-phase SO_2, particulate-phase H_2SO_4 and inorganic sulfates during the thermochemical process.

Table 5 The effect of oxygen input on concentrations of particulate and gas-phase sulfur and nitrogen components in syngas generated from the thermochemical conversion of wood

Oxygen input	Syngas contaminants					
	Particulate sulfates ($\mu g/m^3$)	Gas-phase SO_2 ($\mu g/m^3$)	Ratio sulfates/ SO_2	Particulate nitrates ($\mu g/m^3$)	Gas-phase HNO_3 ($\mu g/m^3$)	Ratio nitrates/ HNO_3
225 ppm	1.4	1.8	0.8	2.2	1.3	1.7
1.0 vol.%	5.6	3.8	1.5	1.4	2.9	0.48
1.6 vol.%	8.1	13	0.6	2.3	11.4	0.20
2.5 vol.%	201	240	0.8	4.8	18.6	0.26

Table 6 Effect of oxygen input on concentrations of aromatic compounds in syngas generated from the thermochemical conversion of wood

Oxygen input	Syngas contaminants						
	Benzene (ppm)	Toluene (ppm)	Xylenes (ppm)	Naphthalene (mg/m^3)	Methyl naphthalene (mg/m^3)	Fluorene (mg/m^3)	Acenapthene (mg/m^3)
225 ppm	5845	3.9	0.0	1.8	0.0	0.0	0.0
1.0 vol.%	960	25	0.21	5.4	0.014	0.004	0.075
1.6 vol.%	1350	44	0.58	38.4	0.31	0.122	1.47
2.5 vol.%	1260	27	0.27	11.3	0.25	0.034	1.54

The concentration of nitric acid increased from 1.3 to 18.6 $\mu g/m^3$ when the concentration of O_2 was increased from 225 ppm to 4.1 vol.% (Table 5). HNO_3 was probably formed from oxidation of NH_3, NO and NO_2 in the syngas. However, the concentration of particulate nitrates did not increase substantially. This is probably due to the fact that potassium nitrate and sodium nitrate decompose at 400 and 380 °C, respectively, which is well below the operating temperatures of the thermochemical conversion system [27].

Although nitrogen in the wood feedstock is in much higher concentration than sulfur (Table 2), the concentration of sulfates in the particulates was found to be several times greater than nitrates (Table 5). These data are consistent with previous studies [28], which reported that the pyrolysis of wood in the presence of oxygen forms particles that primarily comprised potassium and sulfate as a result of the following reaction.

$$2KOH + SO_2 + 1/2O_2 \rightarrow K_2SO_4 + H_2O$$

Table 5 also summarizes the effect of O_2 concentrations on the ratios of particulate to gas-phase sulfur and nitrogen species in the syngas. It is shown that increasing O_2 in the thermochemical conversion process did not have a significant effect on the ratio of these particulate to gas-phase species.

Table 6 summarizes the effect of O_2 on the concentrations of benzene, toluene, xylenes and selected polynuclear aromatic hydrocarbon (PAH) compounds in the syngas. There was a decrease in the concentration of benzene by about six times when O_2 was increased from 225 ppm to

1.0 vol.%. The benzene concentration then stayed relatively constant from 1.0 to 2.5 vol.% O_2. In contrast, the toluene and xylene concentrations increased when the O_2 was increased from 225 ppm to 1.0 vol.% but then stayed relatively constant from 1.0 to 2.5 vol.%. O_2.

The concentrations of the PAH compounds (naphthalene, methyl-naphthalene, fluorene, and acenapthene) also increased by several times as O_2 increased from 225 ppm to 2.5 vol.%. At temperatures above 100 °C, these four PAH compounds are present entirely in the gas-phase, whereas at 25 °C (the syngas sampling temperature) they are distributed between the particulate and gas-phase [15–17]. Therefore, these specific PAH compounds will not act as poisons in catalytic reactions, or cause fouling of engines and turbines, in applications where operating temperatures exceed 200 °C.

Table 7 summarizes the effect of O_2 on the concentrations of oxygenated PAH compounds in syngas. As expected, an increase of O_2 in the integrated solid and gas-phase steam reforming processes significantly increased the concentration of these oxygenated PAH. High concentrations of these oxygenated PAH have also been reported in particulates generated from diesel engines [17]. Since diesel engines operate with excess O_2, their chemistry of formation is expected to be comparable to this thermochemical process.

Table 8 summarizes the effect of O_2 on the concentrations of formaldehyde, acetaldehyde and benzaldehyde in the syngas. An increase of O_2 in the thermochemical process reduced the concentrations of these three aldehydes by

Table 7 Effect of oxygen input on concentrations of oxygenated-PAH derivatives in syngas generated from the thermochemical conversion of wood

Oxygen input	Syngas particulate-phase contaminants ($\mu g/m^3$)			
	Hydroxy-naphthalenes	Dihydroxy-naphthalenes	Dihydro-inden-2-ones	Benzo-pyranones
225 ppm	0.0	0.0	0.0	0.0
1.0 vol.%	288	97	32	105
1.6 vol.%	930	311	90	131
2.5 vol.%	732	244	83	195

Table 8 Effect of oxygen input on concentrations of gas-phase aldehydes in syngas generated from the thermochemical conversion of wood

Oxygen input	Syngas gas-phase contaminants (ppb)		
	Formaldehyde	Acetaldehyde	Benzaldehyde
225 ppm	2.1	365	9.3
1.0 vol.%	1.0	47.5	0.6
1.6 vol.%	0.7	109	3.7
2.5 vol.%	1.4	199	3.5

Table 9 Effect of oxygen input on concentrations of elemental species in syngas particulates generated from the thermochemical conversion of wood

Oxygen input	Syngas particulate contaminants ($\mu g/m^3$)			
	Calcium	Silicon	Potassium	Sodium
225 ppm	0.0	1.6	0.3	23
1.0 vol.%	1.4	1.3	9.0	–
1.6 vol.%	6.4	9.8	27	4
2.5 vol.%	32	8.6	128	15
4.1 vol.%	86	91	127	20

nearly two times. This is not surprising since these aldehydes are in a partially oxidized chemical state, and further oxidation will result in the formation of formic acid, acetic acid and benzoic acid.

Table 9 summarizes the effect of O_2 on the concentrations of particulate calcium, silicon, potassium and sodium in the syngas. It was found that an increase of O_2 in the integrated solid and gas-phase steam reforming processes results in a significant increase of particulate calcium, and potassium species in the syngas, but not sodium species. This is probably because calcium and potassium are 10 and 6 times more abundant than sodium in the wood feedstock (Table 2).

The data in Table 10 demonstrate that an increase of O_2 from 1.6 to 2.5 vol.% in the integrated solid and gas-phase steam reforming processes significantly reduced the concentrations of four easily oxidized, unsaturated gas-phase hydrocarbons: 1,3-butadiene, acetylene, propene, and ethene. The decrease in abundance (due to oxidation) of these hydrocarbons was highest for 1,3-butadiene (the most reactive species) and lowest for ethene, which is in agreement with previously reported data from laboratory oxidation studies [24–26].

Table 11 summarizes the average concentrations of contaminants from the plant operating over a period of 3 days at an average O_2 system concentration of 225 ppm. These data were obtained from syngas sampled after the final polishing (purification) step. As shown here, the average concentrations of key contaminants in the syngas

were very low when the O_2 input concentrations in the system were maintained below 500 ppm.

Table 12 summarizes the distribution of plant carbon inputs and outputs generated from the conversion of 1000 kg of biomass carbon to products and the carbon mass balances for the TCC and LFP systems as well as the total integrated plant. The primary products from the TCC conversion of wood include syngas, biochar and organic contaminants removed from the syngas by the water scrubber. The total carbon quantified in these products represented 97.7 % of the carbon input into the TCC.

Discussion

It has been demonstrated that the presence of O_2 during thermochemical processes has a significant effect on the formation of syngas contaminants. The concentration of particulate organic carbon compounds increased from 3.3 to 122 mg/m^3 and particulate elemental carbon increased from 0.6 to 98 mg/m^3 when O_2 was increased from 225 ppm to 4.1 vol.%. It is proposed that free-radical oxidation of hydrocarbon gases during the thermochemical process is a primary chemical mechanism for the formation of high molecular weight polynuclear aromatic hydrocarbons, oxygenated hydrocarbons and polymeric materials, which are commonly referred to as organic particulate contaminants. These chemical mechanisms were confirmed

Table 10 Effect of increased oxygen concentration (1.6–2.5 vol.%) on the reduction of unsaturated, gas-phase hydrocarbons relative to ethane in syngas generated from the thermochemical conversion of wood

Syngas component	Decrease in syngas constituents relative to concentration of ethane			
	1,3-Butadiene	Acetylene	Propene	Ethene
Relative concentration decrease with increased oxygen	9.3 times	5.2 times	4.5 times	3.4 times

Table 11 Average concentrations of contaminants (after unit operation #4b) from the pilot IBR plant operating with less than 500 ppm oxygen input compared to maximum recommended contaminant levels for catalytic conversion of syngas to liquid fuels

Catalyst contaminants	3-Day average syngas contaminant concentrations	Maximum recommended contaminant levels
Hydrogen sulfide (H_2S) and carbonyl sulfide (COS)	0.1 ppb	<20 ppb
Sulfur dioxide (SO_2)	0.7 ppb	<20 ppb
Oxygen (O_2)	225 ppm	<500 ppm
Ammonia (NH_3)	53 ppb	<75 ppb
Hydrogen chloride (HCl)	<0.2 ppb	<35 ppb
Nitric acid (HNO_3)	5 ppb	<50 ppb
Total particulate matter (PM)	25 $\mu g/m^3$	<500 $\mu g/m^3$

Table 12 Distribution of plant carbon inputs and outputs generated from the conversion of 1,000 kg of biomass carbon to carbon containing products

Components	kg of C in TCC products
H_2	0.0
CO	417.0
CH_4	285.0
CO_2	122.6
C_2–C_5 HCs	4.2
Biochar	135.5
C in scrubber water	13.0
Total kg carbon	977.3

by studying the concentrations of selected oxygenated hydrocarbons formed from this plant.

The biomass thermochemical conversion processes described herein use heat, pressure and steam (in the absence of air). These processes encompass a complex set of reactions involving the formation, propagation and termination of radical species for which there are numerous free-radical pathways. It is well known that hydrogen (H^*), hydroxyl (OH^*), oxy (O^*) and hydroperoxy (OOH^*) radicals are important reactive intermediates in these high-temperature oxidation processes [24–26] as shown by reactions (1)–(5). In addition, reaction of the hydroxy

radical with methane is the predominant formation process for methyl (CH_3^*) radicals, as shown by reaction (6).

$$H_2 \rightarrow 2H^* \qquad (1)$$

$$H_2 + O_2 \rightarrow 2OH^* \qquad (2)$$

$$H^* + O_2 \rightarrow O^* +^* OH \qquad (3)$$

$$O^* + H_2 \rightarrow OH^* + H^* \qquad (4)$$

$$H^* + O_2 \rightarrow OOH^* \qquad (5)$$

$$CH_4 + {}^*OH \rightarrow CH_3^* + H_2O \qquad (6)$$

Table 3 shows that the H_2 concentration decreased from 49 to 37 vol.% when the O_2 input was increased from 225 ppm to 4.1 vol.%, which we propose is the result of reactions (2), (3) and (5). The CH_4 concentration decreased from 12 to 9 vol.% as O_2 increased from 225 ppm to 4.1 vol.%, as an outcome of reaction #6.

The abundant primary radical (*) species H^*, OH^*, O^*, CH_3^* and OOH^* react with the myriad of organic compounds in the syngas at varying rates and high reforming temperatures. For example, the abundant hydrogen radical reacts rapidly with benzene to form a benzyl radical as shown by reaction (7). Since benzene is a major constituent in the syngas (Table 6), this is likely the major source of $C_6H_5^*$.

$$C_6H_6 + H^* \rightleftarrows C_6H_5^* + H_2 \qquad (7)$$

These benzyl radicals react quickly with hydroxy radicals to form phenol (reaction 8). Phenol may also be

formed by the reaction of two hydroxy radicals with benzene (reaction 9).

$$C_6H_5^* + OH^* \rightleftarrows C_6H_5OH \qquad (8)$$

$$C_6H_6 + 2OH^* \rightarrow C_6H_5OH + H_2O \qquad (9)$$
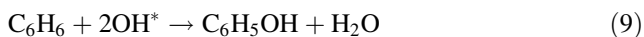
Since reaction #8 is a reversible process, the addition of higher concentrations of OH* and their subsequent reaction with $C_6H_5^*$ helps drive reaction (8) to the right. The data in Table 6 help validate these reaction paths since benzene is reduced from 5845 ppm when O_2 is 225 ppm to an average of 1150 ± 200 ppm when 1.0–2.5 vol.% of O_2 is present.

The benzyl radicals may also react with CH_3^* to produce toluene (reaction 10). As a result, toluene increased from 3.9 ppm at 225 ppm of O_2 to an average of 32 ± 10 ppm when 1.0–4.1 vol.% of O_2 is present, which further supports this reaction path.

$$C_6H_5^* + CH_3^* \rightarrow C_7H_8 \qquad (10)$$

In a similar fashion, the hydroxy radicals react with other aromatics, polycyclic aromatics, alkanes, and alkenes to form hydroxy and di-hydroxy derivatives. As a result, thermochemical processes that use oxygen or oxygen/steam mixtures produce organic particulate contaminants that contain high concentrations of phenolics such as phenol, cresol, xylenols and ethyl-phenols [23].

Table 7 summarizes the concentrations of the hydroxy and di-hydroxy derivatives of naphthalene. As expected, the concentrations of these compounds increased rapidly as the concentration of oxygen in the process was increased.

Higher molecular weight PAH may be formed from the reaction of $C_6H_5^*$ with lower molecular weight PAH. For example, pyrene ($C_{16}H_{10}$) can be formed from naphthalene ($C_{10}H_8$) and $C_6H_5^*$ as shown by Eq. (8) and benzo (a) pyrene ($C_{20}H_{12}$) from pyrene ($C_{16}H_{10}$) and $C_6H_5^*$ as given by Eq. (9) [20].
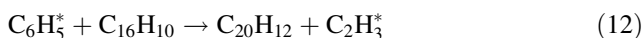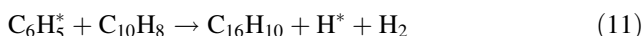
$$C_6H_5^* + C_{10}H_8 \rightarrow C_{16}H_{10} + H^* + H_2 \qquad (11)$$

$$C_6H_5^* + C_{16}H_{10} \rightarrow C_{20}H_{12} + C_2H_3^* \qquad (12)$$

The importance of these oxidation processes was further confirmed by studying the decrease of other easily oxidized hydrocarbons. For example, the concentrations of the highly reactive alkenes and alkyl dienes; 1,3-butadiene, acetylene, propene and ethene decreased by 9.3, 5.2, 4.5

and 3.4 times, respectively, when the O_2 concentration was increased from 1.6 to 2.5 vol.%.

The hydroxy radicals (OH*) and hydroperoxy radicals (HO$_2$*) also react with CO according to reactions 10 and 11.

$$CO + OH^* \rightarrow CO_2 + H^* \qquad (13)$$

$$CO + OOH^* \rightarrow CO_2 + OH^* \qquad (14)$$
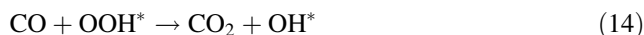
These reactions are substantiated by the data in Table 3 which show that the CO concentration dropped from 23 to 17 vol.% as O_2 increased from 225 ppm to 4.1 vol.%, with a corresponding increase in CO_2 (17–23 vol.%).

Conclusions

It has been demonstrated that the thermochemical process described in this paper, when operated at a nominal oxygen concentration of 225 ppm, produces much lower concentrations (~ 3.9 mg/m^3) (sum of organic and elemental carbon in Table 4) of particulate contaminants than the traditional thermochemical conversion systems described in the literature.

For example, the National Renewable Energy Laboratory (NREL) compared the concentrations of particulate contaminants in syngas from several types of thermochemical conversion systems that employ air or O_2 [8]. It was concluded that average total particulate contaminant concentrations are approximately 1000, 10,000, and 100,000 mg/m^3 for typical fluidized bed, downdraft, and updraft systems, respectively (Table 13). In a more recent study, Stark et al. measured 2000–50,000 mg/m^3 of organic particulate contaminants from their air-blown, fluidized bed biomass gasification system [18].

In addition to tar formation, the presence of oxygen in the thermochemical process has other adverse effects on the efficiency of the integrated biorefinery when oxygen is increased from 225 ppm to 4.1 vol. % (Table 3) as follows:

1. A reduction in [CO] and [H$_2$] of 26 and 24 %, respectively. Since CO and H$_2$ are the primary chemical species that produce fuels and chemicals, the production efficiency of these products will be reduced by about 25 %.

Table 13 Concentrations of particulate components in syngas generated from the pilot IBR plant compared to other types of thermochemical systems (before syngas purification processes)

Total particulate contaminant concentrations (mg/m^3)			
This study 2-stage steam reforming TCC system (225 ppm% O_2 input)	Typical fluidized bed system (with air input)	Typical downdraft system (with air input)	Typical updraft system (with air input)
3.9	1000	10,000	100,000

2. An increase in $[CO_2]$ of 26 % and an increase in $[N_2]$ from <0.20 vol.% to 15.3 vol.%. Since CO_2 and N_2 are diluents in the catalytic reaction, this increase from 29 vol.% to 47 vol.%, requires that the volume of the catalytic reactors will need to be increased by about 38 % at significant additional cost.

This effect of O_2 on H_2/CO ratios has also been studied by Karimipour et al. [29], who varied O_2/steam ratios in a fluidized bed gasifier. They measured H_2/CO ratios of 0.81, 1.02 and 1.27 at O_2/steam ratios of 2.0, 1.0 and 0.75, which demonstrates that increasing levels of O_2 reduce the concentrations of H_2 and CO during thermochemical conversion processes.

Another potential problem with the presence of O_2 in thermochemical processes is the effect of residual oxygen in the syngas on the catalysts used for the production of fuels and chemicals. Since these catalysts need to be kept in a reduced state for the efficient production of fuels and chemicals from [CO] and $[H_2]$, any residual oxygen in the syngas will quickly re-oxidize these reduced catalysts to their non-reactive, oxidation state, resulting in reduced fuel production efficiency and potential damage to the catalysts.

The thermochemical process shown in Fig. 1 was upgraded from about 4.5–22 metric ton/day capacity during 2011 and was tested for a total of 1170 h on wood and rice hull feedstocks during 5/2012 to 9/2013. It was found that fuel productivity increased slightly from 53.0 gallons/1000 lbs. to 56.6 gallons/1000 lbs. of biomass carbon during this test period, which confirmed that oxygen and the other syngas contaminants listed in Table 1 were kept at low levels and had no discernible effect on the direct fuel production catalyst.

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests

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Dennis Schuetzle is Chief Technology Officer for Greyrock Energy (http://www.greyrock.com) and President of the Renewable Energy Institute International (http://www.reiinternational.org). He has 41 years of experience in managing scientific and engineering research, product development and manufacturing, renewable energy and fuel production processes, and environmental science and technology programs in collaboration with organizations in North America, Asia, Europe, South America, Russia and South Africa. Prior to his positions with Greyrock and REII, he was Director/Vice President of International Research and Technology (IR&T) for Ford Motor Company from 1994–2003. He has published 113 scientific and engineering papers, edited four books, contributed to 76 technical books and received 12 patents. He is the recipient of 11 international awards including five RD100 awards for the successful commercial deployment of new technologies into the global marketplace. Dr. Schuetzle obtained Ph.D.s in Chemistry and Civil and Environmental Engineering from the University of Washington, a MS degree from Stanford in Chemical Physics/Computer Science, and a BS degree in Chemistry from California State University—San Jose.

Robert Schuetzle is the President of Greyrock Energy (http://www.greyrock.com). His company is currently managing the deployment of commercial plants in the US and Canada for the conversion of natural gas and natural gas liquids to synthetic diesel fuel. He recently completed DOE demonstration projects for the conversion of biomass to drop-in fuels and solar reforming of carbon dioxide to produce diesel fuel. Prior to this leadership position with Greyrock, he was as a Principal with EMC Corporation and also a Consultant for Accenture in which he managed strategy and technology projects for clients in the Americas, Europe and Asia-Pacific. He was awarded EMC's prestigious award for his efforts related to new market development. During 1998–2000 was CEO of Digitella Technology in which he developed and patented the key technologies that have made it possible for cell phones and other devices to acquire, store and transmit digital media. Mr. Schuetzle obtained his B.S. in Mechanical Engineering from the University of Michigan and Computer Engineering Specialty from the University of New South Wales, Australia. He is a frequent industry speaker, has published several technical papers on renewable energy and renewable fuels, and holds seven patents.

S. Kent Hoekman is a Research Professor at the Desert Research Institute (DRI) in Reno, Nevada (http://www.dri.edu.). His research interests include development of renewable energy systems, conversion of biomass to biofuels, environmental impacts of fuels and energy systems, and air quality impacts of vehicle emissions. He has 35 years of experience in defining, conducting, and managing scientific research in these areas. Prior to joining DRI, Dr. Hoekman spent 21 years at Chevron, where he focused on technical and regulatory issues related to transportation fuels, mobile source emissions controls, vehicle technology, and urban air quality. He obtained a Ph.D. in Organic Chemistry from Iowa State University, and a B.S. in Chemistry from Calvin College.

Barbara Zielinska is an Emeritus Research Professor at the Desert Research Institute (DRI). Her research interests include sampling and analysis of trace organic species present in the atmosphere (both gas-phase and particle-phase), development of analytical methods to characterize primary and secondary organic aerosols, kinetics and products of gas-phase reactions of organics, and characterization of organic emissions from mobile and stationary sources. For 25 years, Dr. Zielinska served as Director of DRI's Organic Analytical Laboratory (OAL). Prior to joining DRI, she worked at the Statewide Air Pollution Research Center at U.C. Riverside. She obtained a Ph.D. in Chemistry from the Polish Academy of Sciences and a M.Sc. in Chemistry from the Technical University of Lodz, Poland.