Spectroscopic Diagnostics and Material Characterization for Wave Liquefaction™ Processing of Carbon Materials for the Production of Value-Added Chemicals and Feedstocks

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ABSTRACT

This paper presents optical spectroscopic diagnostics in H Quest Vanguard's microwave-plasma technology applied to coal and material characterization results from its application to H_2 generation from natural gas. Plasma diagnostics for process control will be illustrated. Chemical analyses are presented of CTL products. Recent results yielding nanographene as a premium carbon by microwave-plasma processing of methane will be shown.

Keywords: Microwave, Hydrogen, Premium Carbons, Graphene, CTL

1 INTRODUCTION

Microwave-driven plasma-mediated reaction engineering represents process intensification for energy efficient and economical hydrocarbon conversion processes. Examples include coal-to-liquids and natural gas conversion to hydrogen and premium carbon products. Optical emission spectroscopy and analysis provides species identification and determination of temperatures in different energy modes in the non-equilibrium plasma.

2 MATERIALS AND METHODS

Microwave energy, variable between 1- 4 kW is -coupled into a continuous flow reactor. Wave Liquefaction™ process applied to coal implements in-situ product upgrading via hydrogenation and/or methylation reactions enabled by activating hydrogen or methane present in the process gas. Pulverized coal is fed by a particle seeder. Gas ratios are optimized for the particular hydrocarbon feedstock conversion. An alternative application of the microwave plasma processing is methane decomposition to H_2 and premium carbon products. Reactor residence times are sub-second and performed at atmospheric pressure. Filters, traps and cyclone stages downstream of the reactor perform gas/liquid/solid separations.

2.1 Optical Emission Spectroscopy

Spectroscopic data collection was performed using a fiber-optically coupled Ocean Optics HR2000 spectrometer fitted with a UV-NIR grating for a spectral range of 900 nm. All optical emission spectra are spectrally calibrated using a Hg/Ar lamp and corrected for instrument response function using a NIST-traceable tungsten lamp as spectral calibration standard. Temperatures of C_2* are determined using custom spectral band-fitting algorithms, taking into account the electronic baseline and underlying blackbody radiation. Spectral fits are performed at 1 nm spectral resolution. Carbon particle temperatures are determined by fitting Planck's radiation law with black body conditions. Ar* emission lines are identified by reference to the NIST spectroscopic database.

2.2 Gas/Liquid/Carbon Analyses

A suite of characterization tools have been applied to the light gases, liquid and solid carbon products. Gas and liquid analyses were performed using gas chromatography-mass spectrometry. For the solid carbon products SEM has been applied to coal chars for cenosphere analysis, and for the carbon products from methane decomposition, scanning electron microsocpy (SEM) for morphology, transmission electron microscopy (TEM) for (nano)structural assessment and identification of different carbon forms (i.e. sp^2 phases), X-ray diffraction (XRD) for evaluation of graphitic structure, thermo-gravimetric analysis (TGA) for bulk determination of oxidative reactivity of the carbons as a means by which to assess graphitic content and gas (N_2) adsorption analyses for texture – i.e. surface area and porosity. Elemental analysis was also performed for HCNS and O by difference.

3 RESULTS AND DISCUSSION

Optical diagnostics are central to reaction characterization and hold particular value for species identification and temperature determination [2]. Observed intensity ratios or spectra band shapes can yield temperature by Boltzman analysis using spectral constants. Moreover, optical emission serves to identify reactive species and intermediates, albeit indirectly inferred by the observation of their electronically excited counterparts, e.g. CH* and C_2* radicals. For example, the presence of key atomic or diatomic radicals can support postulates of electron impact dissociation, and radical mediated bond insertion or radical capping reactions and provide mechanistic insights from the temperatures associated with the different degrees of freedom – electronic, vibrational, such as from the C_2* ($d^3\pi_g$ – $a^3\pi_u$) Swan band emission. As illustration, Fig. 1 shows an optical emission spectra of C_2* ($d^3\pi_g$ – $a^3\pi_u$) from the H Quest MW pilot scale reactor (with addition of CH_4 and H_2 to the process gas feed) along with simulated spectra for the indicated temperatures, where the fitting resolution is 1 nm.

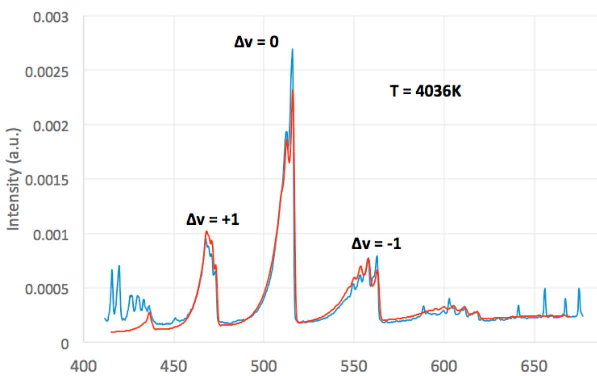

Figure 1. Swan band emission from C_2 (blue) and simulated spectra fit (red) for T = 4036 K.

Microwave (MW) activated natural gas decomposition for H_2 generation produces no CO_2 and requires zero process water, in contrast to the present industrial process – steam reforming. Notably it opens a path for renewable energy storage by coupling electrical energy into chemical bond energy – with H_2 being particularly versatile as fuel or chemical precursor. Moreover, MW activated natural gas decomposition does not require additional carbon as catalyst but rather produces carbon. Therein MW driven decomposition of methane achieves green hydrogen production and production of value-added carbon materials. Initial assessment of these carbon materials requires characterization by microscopic and spectroscopic techniques. Illustrative examples of carbon products by high-resolution transmission electron microscopy (HRTEM), Raman and X-ray diffraction will be shown – Fig. 2 shows a representative Raman spectrum of the carbon product. Complementary thermo-gravimetric analyses assess the oxidative reactivity of the carbon products. Optical diagnostics such as multi-wavelength pyrometry relate these material characteristics to reactor conditions and can be applied for process control.

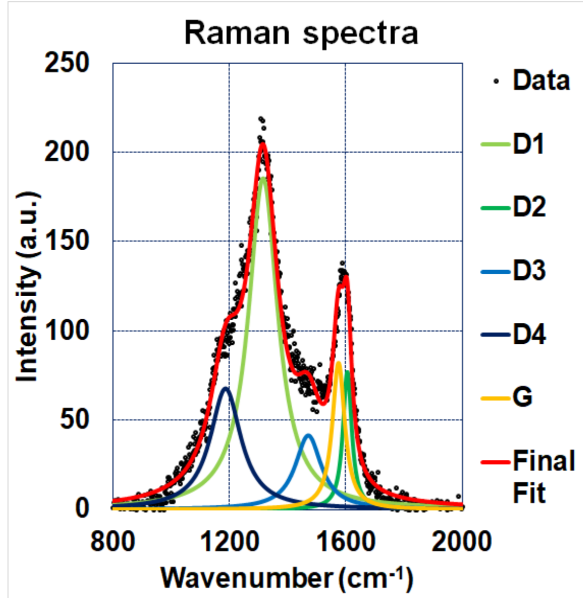

Figure 2. Raman spectrum and 5-fold peak deconvolution of generated carbon product.

4 NEW DEVELOPMENTS

Current methods of producing hydrogen include steam methane reforming (SMR), coal gasification, water electrolysis, biomass gasification and thermochemical processes [1]. Presently, 95% of industrial hydrogen (22.7 million m.t./ year in 2014), is produced via steam-reforming of natural gas [2]. This process is burdened with high CO_2 emissions and water consumption. Pyrolysis is a competitive approach wherein thermally driven decomposition of methane produces H_2 and solid carbon. The carbon can be "naturally" captured as a solid product, and, provided its form has commercial applications, has no sequestration costs and provides economic by-product credit for hydrogen co-production. Despite the relatively low theoretical energy requirement of 78.4 kJ/mole CH_4 converted [3], purely thermal decomposition of methane to hydrogen requires temperatures exceeding 1200°C, which presents operational and energy source challenges. H Quest's microwave plasma pyrolysis process presents a transformational solution to the challenge of efficient, clean, and cost-effective methane decomposition. Unlike other approaches, it does not rely on conventional (contact, convective, or dielectric) heating or use of thermal plasmas. Rather, it employs a microwave resonant cavity to create localized and high-energy reaction zones in the gas as it passes through the reactor's active zone. Results are illustrated by the TEM images in Fig. 3. instead of an amorphous carbon aerosol carbon "soot", a form of nanographene is produced.

Platelets are on the order of a few hundred nanometers with stacking dimensions ranging from 1-6 sheets, typically 3-5 as discerned by offset edges. The stacks are slightly curled as observed in Fig. 3. Often "splotches" are observed at high magnification – interpreted as macromolecular PAH-like precursors to the sheets that agglomerated with larger sheets and/or became trapped between platelets, further growth then being inhibited. Presently the formation and growth of the platelets is believed to proceed via a radical reaction mechanism analogous to the hydrogen-abstraction, acetylene addition (HACA) mechanism well established for soot formation in pyrolysis and combustion [4,5]. The shared commonalities of the present microwave plasma and combustion are the high hydrogen concentration and high temperature – see Fig. 3. Distinghuishing the present system from fuel-rich combustion processes is the microwave radiation and more specifically, the high electron concentration. Moreover, these two factors are synergistic as the electrons, accelerated by the EM field will promote radical formation via electron impact dissocation. Further studies into optimizing product yield and uniformity are presently underway towards scaleup.

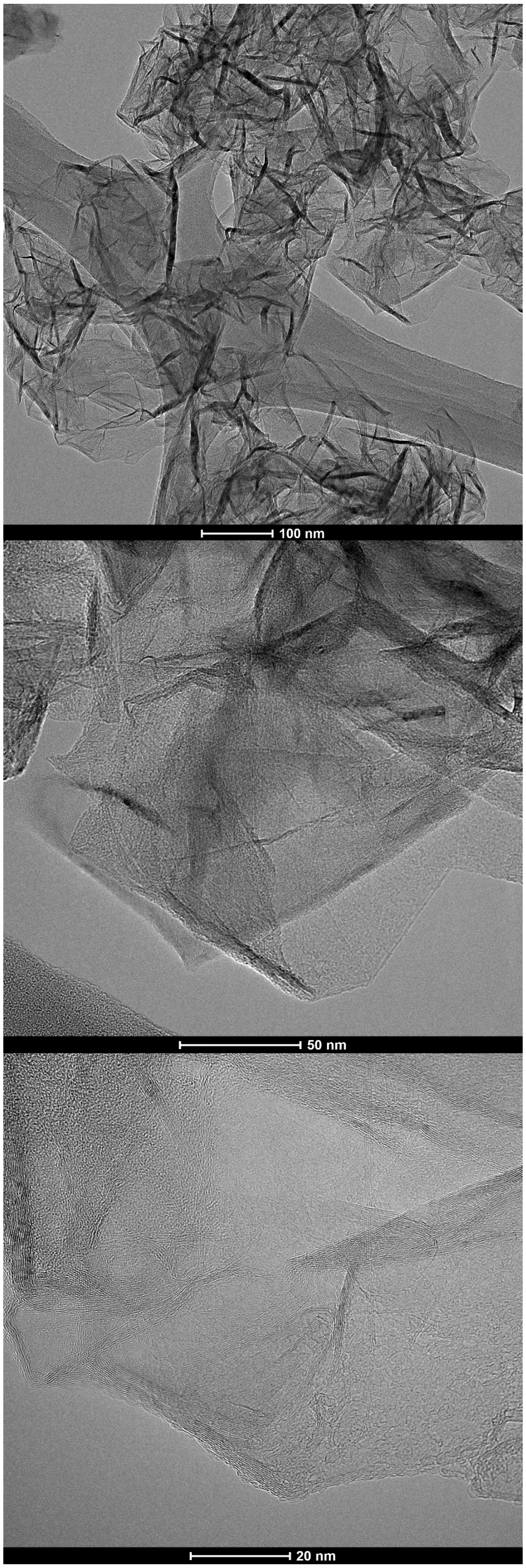

Figure 3. HRTEM images of nanographene produced by Wave Liquefaction process with methane as feedstock.

5 CONCLUSIONS

H Quest Vanguard is developing broad-spectrum microwave plasma processes targeting conversion of hydrocarbon feedstocks such as coal and natural gas to value-added materials, chemicals and fuels [6,7]. It was originally invented responding to the DARPA initiative for GHG-emission-free and cost-effective production of US Air Force jet fuel from the domestic coal resources. Natural gas can be used in single-stage reactor as a hydrogen source, eliminating external hydrogen production units and the associated CO_2 production, water consumption, and capital costs, and providing excess hydrogen sufficient for downstream hydro-treating. The MW process produces fast heating resulting in flash devolatilization and pyrolysis followed by fast quenching, preserving the primary pyrolysis products and volatiles' molecular structure.

Since company formation in 2014, H Quest Vanguard, Inc. has developed ample material base and expertise in development of chemical and catalytic processes enhanced by microwave plasma. In particular, H Quest has developed a conversion process that applies microwave energy to rapidly co-pyrolyze solid hydrocarbons (e.g. coal) and natural gas to produce liquid hydrocarbons. A wide range of carbon materials including graphene and ordered carbon blacks have been observed across a wide range of experiments. These forms have potential for high value applications: electrical conductivity additives for plastics, and as electrode material in supercapacitors and Li-batteries. Ongoing SBIR Phase I projects have demonstrated feasibility of a microwave driven plasma mediated methane decompostion for H_2 production and nanographene formation as a premium carbon.

6 ACKNOWLEDGEMENTS

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