Methane–Carbon Dioxide (CH_4-CO_2) Activated Synergistic Biomass Gasification for Hydrogen (H_2)-Rich Syngas Production

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Conventionally, major source of hydrogen production in the US has been natural gas, a fossil energy source. Transition from fossil fuels to renewable technologies is extremely challenging as renewable energy sources like solar, wind, and biomass are highly unreliable, subject to variation in geography and local climatic conditions. Apart from the technological challenges in utilization of renewable energy sources, they are not cost-effective and their return on investment index (ROI) is quite low. However, there is growing need for CO_X free hydrogen as conventionally produced hydrogen generates high concentrations of CO, CO_2 and require expensive separation units like solvent / sorbent based technologies. Researchers at West Virginia University have developed a novel methane catalytic pyrolysis process which produces CO_X free hydrogen with the formation of high carbon nanotubes (CNTs) and carbon fibers (CNFs) which can be separated from the catalyst and obtained as commercial product or reutilized as an active support for the catalyst. This catalytic methane decomposition (CMD) process utilizes Ni-Pd/CNT catalyst where the CNT is obtained from methane decomposition. Hydrogen production on the Ni-Pd/CNT catalyst was demonstrated over multiple cycles for 180 minutes time on-stream. About 50 to 60% methane conversion was observed in 5 cycles for 180 minutes TOS on the Ni-Pd/CNT catalyst. Transition from fossil hydrogen to renewable hydrogen is bridged by the unique 'natural gas – biomass co-processing. At WVU, hydrogen rich syngas production through renewable hardwood biomass gasification was obtained through synergistic natural gas – biomass co-processing. About 5% methane co-processed with biomass at 850^{o}C on Fe-Mo/CNF catalyst produces H_2:CO ratio of 6 with a very low CO_2 concentration of < 5% in the syngas. About 60 to 80% hydrogen was obtained in the product gas on the Fe-Mo/CNF, Ni-Mo/CNF, and Mo-Pd/CNF catalysts. Synergistic methane activated biomass gasification could be a promising technology for hydrogen rich syngas production as it requires very low concentrations of methane which could be obtained from flare gas. Flare gas is natural gas flared during commissioning of new wells or maintenance of existing wells in shale gas field. On-site utilization of flare gas with biomass could greatly curb CO_2 emission while producing hydrogen rich syngas. CO_2 utilization in the methane activated biomass gasification was studied by adding 1% CO_2 to the gas feed. CO_2 and CH_4 activation at high temperature was performed on Fe, Ni, and Pd active sites while Mo active sites are responsible for deoxygenation of oxygen rich biomass. Adding 1% CO_2 allows for controlled production of syngas with H_2:CO between 2 to 2.5 and CO_2 concentration of 10 to 15%. Syngas with H_2:CO ratio of 2 to 2.5 is ideal for downstream chemical synthesis. In-situ conversion of raw biomass co-processed with 5% methane produces H_2-rich syngas on the carbon nanofiber supported catalyst. CNF support is also obtained from the biomass feedstock by impregnation with metals and pyrolysis at 700^{o}C. This process is 95% renewable with net reduction in CO_2 emissions by recycling of CO_2. Application of renewable technologies is on the rise especially in power generation but is still far from being a mainstream source of hydrogen and power. Development of high efficiency CO_X hydrogen production processes like catalyst methane decomposition and renewable-fossil based processes like synergistic natural gas – biomass co-processing is a logical transition from fossil to renewable hydrogen production.