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Process Development of Shale Gas Assisted Lignin and Biomass Reforming through Novel Reaction Pathway and Catalyst Design To Produce Hydrogen Rich Syngas for Fuels and Value Added Chemicals

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**Process Development of Shale Gas Assisted Lignin and Biomass
Reforming through Novel Reaction Pathway and Catalyst Design To
Produce Hydrogen Rich Syngas for Fuels and Value Added Chemicals**

Amoolya D. Lalsare

Dissertation submitted
to the Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
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Abstract

Process Development of Shale Gas Assisted Lignin and Biomass Reforming through Novel Reaction Pathway and Catalyst Design To Produce Hydrogen Rich Syngas for Fuels and Value Added Chemicals

Amoolya D. Lalsare

Novel biomass reforming strategy through synergistic co-processing with flare gas (methane and carbon dioxide) was developed at West Virginia University. Hardwood biomass comprised of lignin, hemicellulose, and cellulose is abundant in the US and potentially a sustainable source of hydrogen through extensive reforming and gasification. Ever-increasing shale gas production in the US occasionally leads to flaring owing to stranded production across the US. Achieving biomass co-processing with natural gas about to be flared in such stranded shale plays is the underlying motivation here. A novel reaction pathway was discovered wherein methane and carbon dioxide assisted reforming of biomass could be performed in a modular fashion to obtain hydrogen-rich syngas. Laboratory scale fixed bed reactor setup and bench scale bubbling fluidized bed setup were developed for showcasing the synergy in catalytic co-processing of ligno-cellulosic biomass with flare gas. Highly active metal-metal carbide dispersed catalyst supported on graphene (GNS) / carbon nanofibers (CNF) was developed and evaluated. Transition metal (Fe, Ni, Pd) doped Mo_2C nanoclusters dispersed on GNS / CNF support showed considerably better activity than traditional ZSM-5 supported catalysts and showed excellent resistance to deactivation over multiple reaction cycles through self-regeneration. This laboratory-scale synergistic reforming approach was scaled up to a bench scale semi-continuous bubbling fluidized bed reactor. With a reactor bed ID of 1.5 inch, a fluidized bed reactor would allow for higher throughput of biomass with CH_4 / $\text{CH}_4 - \text{CO}_2$ in the fluidizing gas. Lignin and ligno-cellulosic hardwood biomass were the two feedstocks chosen for reforming based on their higher oxygen content.

Reforming of lignin and hardwood biomass was performed through extensive hydrodeoxygenation (HDO) using methane as source of atomic hydrogen. In the initial investigation of methane (primary natural gas component) assisted synergistic biomass gasification was performed on iron-molybdenum (Fe-Mo) supported on ZSM-5 (zeolite) support. Non-oxidative gasification of

biomass on the FeMo-ZSM-5 catalyst at 850°C and 950°C produced syngas with CH₄ concentration >55%. In the absence of external oxygen source, thermal cracking of ligno-cellulosic components and reverse steam methane reforming (SMR) dominates reaction sequence. With the addition of 5 to 15 vol.% CH₄ balanced with N₂, high hydrogen concentration (>70%) in the syngas and high H₂:CO ratio of 4 to 10 was obtained at 850°C and 950°C on FeMo-ZSM-5. However, the molar yield of syngas was low accompanied by low biomass conversion and higher coke deposition on the catalyst. Coke deposition increased with increasing CH₄ concentration from 5 to 15 vol.% whereas H₂:CO ratio decreased by almost 50% from 7.5 to 3.7 for reaction at 950°C.

Although higher H₂:CO ratio in syngas is desired from biomass reforming, valuable carbon and oxygen in ligno-cellulosic biomass has to be obtained in the syngas to minimize the tar yield, coke formation, char residue, and unconverted carbon lost in the reactor. Methane assisted reforming was thus promoted with the addition of a small amount of CO₂ (1 vol.%) in the reacting mixture. CO₂ activation on Fe active sites in the hydrogen-dominated neighborhood was achieved to cause dry reforming of hydrogen to yield equimolar H₂ and CO. The addition of CO₂ along with 5% CH₄ leads to synergistic bi-reforming of biomass which produces syngas with balanced H₂:CO of 2 to 2.5. Novel catalyst development was performed in this study by replacing the zeolite ZSM-5 support with GNS / CNF support as mentioned above. This novel support was generated by pyrolysis of Fe, Mo impregnated biomass. Contrary to FeMo-ZSM-5, Mo existed as β-Mo₂C and Fe as a mixture of Fe / Fe₃C on the new support. This naturally synthesized metal carbide catalyst showed excellent resistance to deactivation by actively altering the coke deposition mechanism on the catalyst. Catalyst performance was thoroughly evaluated by performing 15 reaction cycles at temperature ranging from 800°C to 900°C for time-on-stream isothermal reaction for 2 hours. Fe loading was changed from 0.5 wt.% to 5 wt.% which predominantly lead to synthesis of graphene support with low Fe concentration and carbon nanofiber (CNF) support with higher Fe loading (2.5, 5 wt.%). Over 15 cycles, Fe / Fe₃C – Mo₂C – GNS / CNF support was discovered to regenerate after 10 to 15 cycles.

Fundamental investigation of methane assisted ligno-cellulosic biomass reforming was performed for molecular understanding of the underlying reaction mechanism and catalyst evaluation by replacing transition metal (Fe) dopant with Ni. Fe and Ni doped Mo₂C-GNS catalysts are being on evaluated for p-cresol as a model feedstock representing the reformed oxygenated components in

ligno-cellulosic biomass. CH₄ assisted p-cresol reforming is being scaled up to alkali lignin and hardwood biomass. Experimental and density functional theory (DFT) based investigation is being used for micro-kinetic modelling of the reforming reactions on Fe-Mo₂C-GNS and Ni-Mo₂C-GNS. Lignin biomass is a major waste by-product from paper-pulp processing and constitutes a major component of the natural feedstock. Lignin reforming through flare gas co-processing is planned to be studied and scaled-up to the bench scale fluidized bed reactor setup along with biomass.

Process scale-up to bubbling fluidized bed reactor setup has been planned to showcase biomass – flare gas synergistic co-processing. A 1.5-inch ID bubbling fluidized bed reactor was designed and developed in collaboration with The Department of MAE department in WVU and National Energy Technology Laboratory (DOE), Morgantown. Preliminary experimental tests for investigation of high-temperature non-reactive fluidization hydrodynamics were performed. Important operation parameters for fluidization like minimum fluidization flowrate and optimum fluidizing gas flow rate were calculated by incorporating the effect of temperature. Minimum fluidization flowrate decreased with an increase in the reactor temperature from 200°C to 800°C by 60 to 70% of that at ambient conditions. Preliminary biomass and coal gasification tests were also performed on the BFB reactor to evaluate the performance of the fluidized bed against a fixed bed. The fluidized bed can be operated at higher efficiency over a fixed bed reactor if stable uniform fluidization is obtained. Stable fluidization was observed through pressure sensing at different locations in the BFB reactor bed along with overall bed pressure drop. Preliminary test results have provided the required groundwork for rapid scale-up of the CH₄ / CH₄ – CO₂ assisted catalytic biomass reforming from lab scale fixed bed to bench scale fluidized bed reactor.

Lab-scale experimental investigation was also performed for non-catalytic and catalytic co-processing of waste plastics, southern pine biomass, and Illinois #6 coal. Biomass-coal-waste plastics gasification to syngas was performed over Fe-Mo₂C-GNS / CNF catalyst and FeOOH-SO₄ catalysts. Co-gasification of biomass, coal, and plastics has recently generated commercial interest for development of novel hydrogen production technologies with net negative CO₂ emissions. Specific mix of waste plastics was selected for co-gasification with coal and biomass. High H₂:CO ratio between 2 to 3 was obtained on the 0.5% Fe-4% Mo₂C-GNS, 5% Fe-4% Mo₂C-CNF, and FeOOH-SO₄ catalysts.

Dedication

This work is dedicated to my guru and my parents

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Chapter 1: Introduction

1.1 Objectives

Ever-increasing demand for energy and detrimental impacts of fossil-based energy sources has presented an overarching challenge before governments and organizations across the globe. Per-capita energy consumption is increasing rapidly across the globe with rapid industrialization, urbanization, and infrastructure development in the emerging regions. US ranks 7th in per-capita energy consumption preceded only by Canada and few small developed nations.[1] China has soared to the first place in overall energy consumption followed by the US and India.[1] Ever-increasing demand for electricity and transportation fuels has motivated researchers across the globe to find solutions for non-fossil fuel based energy sources. In the US, the primary source of energy has shifted from coal to natural gas in the decade.[2] Coal mining, transportation, and consumption has been one of the biggest contributors to greenhouse gas emissions in the past century. Although natural gas provides high efficiency energy conversion to electricity and fuels, transition to completely gas-based power plants has been slow.[2] Conversion of natural gas to gasoline has been rendered economically unviable owing to highly volatile crude oil market with general trend of plateauing oil prices over the last decade. Therefore, although natural gas production has increased rapidly between 2008 to 2019, demand for natural gas often fails to exceed the production capacity leading to concentrated flaring of natural gas and shale gas in large production sites such as Eagle Ford, TX, Bakken, ND, and Marcellus shale basin in West Virginia-Kentucky region.[3] Stranded natural gas production, flaring, and mitigation strategies have been overviewed in the following section. Biomass has been the natural source of energy for humanity since existence. In the present day however, fossil fuels dominate human energy consumption for all activities. Major long-lasting and sustainable shift from fossil fuels to renewable energy sources has to occur through increased biomass utilization. Biomass in the form of waste forest residues, bio-waste, and post-harvest residues from agricultural activities could potentially become the solution for meeting growing energy needs in a sustainable manner. However, the technical challenges and economic challenges of biomass utilization have limited large-scale commercial applications for thermochemical conversion to fuels and syngas. The highly variable composition of biomass, heterogeneity of feedstock, and low energy density present considerable challenge both in terms of technology – reactor design, low selectivity to desired chemicals and fuels, and in

terms of economic viability – high cost of logistics, low return on investment, high capital cost, and low-value product formation. Challenges in biomass utilization and a perspective of recent research in biomass conversion has been illustrated in detail in the following sections.

The primary objective of this research is the development of a modular reactor battery for conversion of biomass to fuels and value-added chemicals in stranded shale production regions via co-processing with shale gas and carbon dioxide. The synergistic co-processing approach investigated and demonstrated here holds immense potential for process development and transition to novel hydrogen production technology platform. Such a modular co-processing unit will not only mitigate flaring in the stranded production sites, but also convert waste forest / grass residues and industrial lignin to value-added chemicals. **Following characteristics of the modular co-processing approach promises economically viable hydrogen and chemicals production platform:**

- Flare gas or waste shale gas feed is available with minimal requirement for infrastructure at the natural / shale gas production site.
- Waste forest residues are abundant especially in the Appalachian region with actual public interest in clearing of forested areas for farming and related activities. This will provide easy access to hardwood and softwood ligno-cellulosic biomass feedstock with support from local authorities.
- Large scale paper-pulp industrial activity in neighboring Canada promises short and steady supply chain in North Dakota for black liquor (lignin) which could be directly bought as solid alkali / Kraft lignin or through on-site black liquor filtration cake.
- Waste grass and post-harvest residues from the vast corn-rich Midwest region ensures abundant availability of solid biomass feedstock in production sites in Texas and other parts of the US.
- Development of a continuous moving bed or fluidized bed gasifier / reformer system for biomass blended with shale gas and nitrogen will ensure high-efficiency gasification / reforming to syngas.
- On-site modular co-processing will require minimal investment for capacity building of utilities such as steam, compressed air, nitrogen, heating fuel (propane / shale gas).
- Unlike other biomass thermochemical conversion to fuel systems including reforming and gasification, synergistic methane assisted, methane-ethane assisted, and methane-carbon dioxide assisted biomass reforming does not require pure H₂, O₂, air, or steam as a reforming or gasifying

agent. This is the most-promising aspect of such co-processing approach in terms of economic viability.

- The one-step modular shale gas – biomass reforming process is capable of generating the desired syngas composition for downstream chemical synthesis processes like methanol synthesis, Fischer-Tropsch synthesis as well as hydrogen purification through Pressure-Swing-Adsorption (PSA). This approach eliminates or minimizes the requirement of downstream hydrogen enrichment and syngas conditioning reactor units.

This research is thus focused on the fundamental aspects of process / reaction engineering of shale gas – biomass co-processing. Biomass hydrodeoxygenation (HDO) and hydrogenolysis reforming which requires pure hydrogen is achieved by utilization methane and ethane (C1, C2) in shale gas along with carbon dioxide for balancing the syngas composition. Initial studies were performed for non-catalytic biomass gasification and devolatilization, decomposition regimes for biomass thermochemical conversion. Proof-of-concept investigation of CH₄ assisted biomass reforming was performed using Fe-M-ZSM-5 catalyst and CH₄-CO₂ assisted biomass reforming over novel Fe-Mo₂C-CNF catalyst. Catalyst design and novel reaction pathway of CH₄ assisted biomass reforming was performed extensively followed by catalyst stability and regeneration studies for novel Fe-Mo₂C-GNS/CNF catalyst. The lab-scale reforming reaction system has been scaled up to a bench-scale bubbling fluidized bed reactor system. Figure 1 shows the major research objectives accomplished in the research presented here.

Major Objectives of Modular Shale gas – Biomass Co-processing Platform Development

Figure 1 Summary of major research objectives for process development of modular shale gas - biomass co-processing platform

1.2 Stranded natural gas flaring and mitigation strategies

Flaring is widely used to dispose underutilized natural gas in stranded regions lacking local infrastructure for shale gas utilization or application as fuel. Gas flaring is practiced regularly at oil exploration sites both onshore and offshore, refineries, natural gas liquefaction terminals, coal mines, and landfills. However, a recent study reported that 90% of the global gas flaring occurs at exploration and production facilities. Associated gas (by-product of oil exploration) is regularly flared due to large pressure changes from deep underground sea / rock bed to earth's surface. Due

to stricter environmental regulations and technology advancement in past decades, much of the associated natural gas is utilized and integrated with other processes. However, gas flaring to the extent of 5000 bcf (billion cubic feet) occurs annually around the globe. This flaring results in 300 million tons of CO₂ released contributing to green-house gas emissions.[4] Dry shale gas production at various plays in the US grew from about 8 bcf per day to 70 bcf per day from 2008 to 2019.[5,6] Shale gas production in stranded regions leads to underutilization and subsequent flaring causing high CH₄, CO₂ emissions[7–9]. Flaring during production and maintenance even in small amounts increases the Global Warming Potential (GWP) of shale gas rendering more polluting than traditional natural gas or LNG. Shale gas flaring increased 46% between 2017 to 2018 from 255 bcf to 470 bcf. Even with flaring mitigation measures in place, stranded shale gas production in sparsely populated US states like North Dakota and West Virginia leads to high concentrated GHG emissions.[10]

Flaring reduction strategies include gas pipeline transport to nearby large population centers, conversion to liquid fuel(gasoline), on-site utilization for heating, electricity generation, or reinjection into the underground strata.[11] However, in stranded large production and exploration sites like Bakken, ND and Eagle Ford, TX with very sparse population and hundreds of miles apart from large population centers, developing infrastructure and logistics for gas transport to high-demand markets is often uneconomical. Due to the recent decline in the crude oil prices, gas conversion to gasoline and diesel (Gas To Liquid – GTL) faces stiff competition with crude oil. Moreover, a GTL processing complex requires high capital investment and can only be operated economically at high-throughput large-scale natural gas production sites. Flare gas at drilling, exploration, and production sites is largely utilized for integrated heat and power generation applications.[12] Thus, flaring of natural gas is frequently practiced to maintain economically viable operation of the exploration, drilling, and production sites in the US and around the globe.

To prevent natural gas flaring, innovative modular technologies are being adopted and tested on pilot basis for on-site conversion of shale gas to chemicals and fuels. One such innovative strategy being deployed for on-site shale gas utilization is electricity generation for operation of remote data centers. Such a Digital Flaring Mitigation (DFM) modular system has been developed by Crusoe Energy for deployment in stranded shale gas wells. The DFM system converts variable shale gas composition to electricity for powering energy intensive computing.[13]

However, application of such technologies is limited by the rapidly growing shale gas production in the United States. Mitigation of shale gas flaring could be achieved through on-site utilization for synthesis of valuable chemicals and hydrogen rich syngas. Thus, modular shale gas-biomass co-processing approach has been investigated extensively from a holistic process development perspective. Proof-of-concept results for blending flare / associated gas with ligno-cellulosic biomass / biomass / waste residues has been explored over a conventional zeolite based catalyst and novel carbon nanofiber based catalyst. Catalytic reforming of biomass and shale gas like feedstocks puts a great onus on their stability and regenerability. Single use catalyst deactivated post-reaction cannot be salvaged from the complex biomass reforming residue which could escalate the operating cost of such modular co-processing. Moreover, expensive catalyst supports and metals which require ex-situ regeneration post-reaction or need replenishment frequently would make such modular co-processing approach economically unviable. Therefore, a novel carbon nanofiber / graphene support derived from the waste biomass feedstock with nanoparticle dispersion of Fe, Mo₂C metal-metal carbides has been designed as a stable in-situ regenerable catalyst for the shale gas assisted biomass reforming process. Detailed catalyst design approach adopted and catalyst regeneration through reforming cycles has been investigated and presented here.

1.3 Challenges of lignin and ligno-cellulosic biomass utilization

Abundantly present lignocellulosic biomass is largely underutilized as well owing to limitations such as variable composition, low energy, and low bulk density[14–16]. There is growing interest in utilization of forest residues, switchgrass, and other waste biomass in the Appalachian region. Kraft lignin, a by-product from paper-pulp industry is mainly used for combustion and heat integration applications in chemicals production. Heteropolymer composition of lignin makes it challenging for conversion to valuable chemicals or liquid fuels. The high oxygen content of lignin leads to poor selectivity and yield of chemicals due to complex hydrodeoxygenation, decarboxylation, hydrogenolysis pathways. Approximately 50 million tons of lignin is annually produced worldwide, of which 98-99% is incinerated for steam production and combustion applications in the paper-pulp industry.[17] Naturally, lignin is found abundantly in the cell wall of hardwood and softwood as a large macromolecule with complex composition. Thus, utilization of residues from deforestation in heavily forested areas in the Appalachain region (West Virginia,

northwestern Virginia, Tennessee, and others) will require successful and economically viable conversion of lignin to fuels and value-added chemicals. Largely, lignin can be characterized as a branched polymer with phenolic hydroxyl groups.[18,19]

Lignin utilization for conversion to valuable chemicals accounts for only 1 to 2% of the total industrial lignin produced from the pulp industry worldwide. Lignin conversion to chemicals through the valorization route requires separation of lignin from ligno-cellulosic biomass, long sequence of delicate and complex reaction chemistry before conversion to ketonic intermediates and long chain hydrocarbons. Heterogeneity of lignin aromatic intermediates and varying bond strengths of C-O functional groups presents significant challenges in the valorization route for fuels and chemicals.[20] Lignin valorization to carbon fibers has gained significant interest owing to wide-ranging applications of carbon fiber materials in aeronautical industry, high performance-high efficiency and low fuel consumption light weight vehicle platforms, various unmanned air-defense applications etc. Carbon fiber materials can be obtained from lignin valorization by removal of H, N, O, and S through high temperature carbonization ($\sim 1000^{\circ}\text{C}$) and full graphitization at temperatures up to 3000°C . However, highly energy intensive processes for conversion of highly impure lignin feedstock to high strength carbon fiber materials limits utilization of lignin.[21]

Thermochemical conversion of biomass to fuels through pyrolysis and gasification has been extensively studied before[22–29]. Syngas generated through conventional biomass gasification contains large concentrations of CO_x products needing post-treatment and H_2 enrichment. Direct hydrogen transfer from methane coupled with hydrodeoxygenation of biomass is a promising in-situ technique to produce hydrogen rich syngas from ligno-cellulosic biomass as reported earlier. Addition of low concentration CO_2 possibly from flared gas allows for controlled $\text{H}_2:\text{CO}$ ratio in syngas[30,31]. Biomass fast pyrolysis and gasification holds good potential for the production of hydrocarbon fuels and value-added chemicals.[32][33] Pyrolysis has been extensively researched and applied for producing bio-fuels for direct use in transportation and related applications.[23,27,34–40] However, the decomposition of the highly aromatic lignin structure in the lignocellulosic biomass leads to formation of bio-oil at temperatures below 700°C . [28,41,42] Bio-oil is high in oxygen content and has limited application as fuel owing to high acidity, poor resistance to extreme weather conditions, and instability.[32][43] The thermochemical conversion

of biomass to energy and fuels have been extensively studied for the past few decades.[44][45] Biomass decomposes rapidly between 400°C to 600°C giving devolatilization components like carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), bio-oil, aerosols, and bio-char.[28,32,33,46] High oxygen to carbon weight ratio in lignin and ligno-cellulosic biomass requires hydrogen assisted extensive hydrodeoxygenation to produce lighter oxygen free olefins. Requirement of large throughput of pure hydrogen renders biomass reforming uneconomical in most scenarios.

Moreover, crude oil prices have been highly volatile recently and occasionally dropped below \$40 per barrel.[47] Below the \$40 per barrel price of crude oil, biodiesel production from biorefineries becomes uneconomical (non-profitable).[48] Naturally, for other technologies like methane to gasoline and biomass to bio-diesel, it is nearly impossible to compete with traditional fossil fuel based technologies with already thin profit margins. In-situ tar cracking, hydrodeoxygenation (HDO), and rearrangement to form ketonic intermediates leading to alkanes are typical reaction steps necessary for conversion of biomass to valuable chemicals.[49–51] Transition metals on catalytic surfaces like zeolite (HZSM-5), SiO₂, γ -Al₂O₃ have been studied to initiate biomass upgradation reactions like dehydration, rearrangement, decarboxylation, decarbonylation, and hydrodeoxygenation.[49,52,53] However, poor selectivity of desired products, requirement of high-pressure hydrogen, and the catalyst instability / deactivation increases the cost of the process, rendering it economically unviable.

Novel reaction pathway utilizing biomass and flare gas has been proposed in this study to promote modular on-site biomass – flare gas synergistic co-processing to produce hydrogen rich syngas as a precursor to fuels and value-added chemicals. Syngas with higher hydrogen concentration (>60%) has significantly higher energy output (HHV) compared to CO_x syngas. With >60% hydrogen concentration and ~20% CO concentration, HHV of biomass generated syngas can be as high as 17 MJ m⁻³, up to 50% higher than traditional syngas HHV (~10 to 13 MJ m⁻³). Syngas combustion for power generation is one of the many applications from biomass – flare gas co-processing. Other important applications of hydrogen rich syngas include downstream synthesis of valuable liquid chemicals like methanol, benzene, toluene, xylene, ethyl benzene through methanol synthesis, Fischer Tropsch (F-T) synthesis. Hydrogen rich syngas can be an important precursor for ammonia synthesis which traditionally requires CO_x free hydrogen in large feedstock

throughput. Figure 2 shows the process schematic of proposed modular shale gas-biomass co-processing reactor battery for conversion to hydrogen rich syngas. Proposed process of co-processing biomass with flare gas to achieve hydrodeoxygenation (HDO) reforming and production of hydrogen rich syngas by-passes expensive and poor selectivity biomass reforming processes. Hydrogen rich syngas with HDO conversion up to 80% can be achieved through this synergistic co-processing concept. Following sections illustrate the novel process in detail from conceptualization to catalyst development and process scale-up.

1.4 Overview of biomass to syngas and current hydrogen enrichment processes

Nishikawa et al reported that, at 900°C, high-catalyst-to-biomass loading of 40% was effective in tar cracking and high-purity hydrogen production.[54] Ni nanoparticles on MCM-41 supports were utilized for biomass gasification to enhance hydrogen production.[55,56] Use of a suitable catalyst for biomass gasification increased the H₂:CO ratio in syngas from 1.15/2.15 to 1.87/4.45.[57,58] Coconut-shell gasification was performed with steam on Pt, Fe, and Co promoted catalysts and it was reported that the use of Fe promoted catalysts increased hydrogen and carbon monoxide composition by improving the water gas shift reaction.[59] This ratio can be increased by fast pyrolysis / gasification of biomass with a hydrogen-rich source like methane. H/C_{eff} ratio of biomass is about 0.3, which is not suitable for producing hydrogen-rich syngas for production of value-added chemicals. Methane that comes from an inexpensive and abundant source like natural gas has a very high H / C_{eff} ratio of 4.[60] In recent years there have been efforts to utilize methane and biomass in a single reactor but mainly for the purpose of fast pyrolysis. In one of the recent studies, pine saw dust biomass was impregnated by Ni and gasified with steam at 600°C to produce H₂ rich syngas with maximum H₂ yield of 60% in the outlet gas. Steam was replaced by methane to perform catalytic methane decomposition (CMD) for 10 hours at 850°C on Ni/carbon catalyst to further increase H₂. About 90% methane conversion was reported with the process.[56] The proposed novel co-processing concept focuses on non-oxidative catalytic gasification in a single stage using co-feed of methane (5 - 15 vol.%) with biomass.

1.5 Methane – carbon dioxide assisted biomass reforming

Methane assisted biomass reforming over Fe-Mo-ZSM-5 (zeolite) support was showcased as a proof-of-concept for the synergistic co-processing of flare gas and biomass. Methane assisted biomass reforming is mainly achieved through thermal catalytic activation of CH₄ possibly over

Fe sites and subsequent hydrodeoxygenation of oxygenated components in lignin, hemicellulose, and cellulose. Methane activation acts as a hydrogen source for HDO reforming of biomass. Liberated oxygen on Mo / Mo₂C forms steam adsorbates which reform carbonaceous components in biomass through steam reforming, water-gas shift reactions. Hydrogen dominant syngas is produced with H₂ concentration between 60% to 80% and high H₂:CO ratio of 3.5 to 10. However, downstream chemical synthesis processes require balanced H₂:CO in syngas between 2 to 3. Thus, CO₂ was considered as ideal candidate for limited oxygen source through thermal catalytic activation. Carbon dioxide is one of the most stable products of a process and is difficult to activate thermodynamically[61–63]. However, carbon dioxide can be activated in several ways of which high-temperature activation of carbon dioxide on active metal sites is key for CO₂ utilization in this study[64,65]. This activation involves electron transfer from metal to CO₂ to form CO₂⁻ radical. Lower atomic number transition metals are reported to be better for high-temperature CO₂ activation[66–70]. This could be due to partially filled 3d and 4s orbitals of lower atomic number transition metals like Fe ([Ar] 3d⁶ 4s²), Co ([Ar] 3d⁷ 4s²), Ni ([Ar] 3d⁸ 4s²), Cu ([Ar] 3d⁹ 4s²). In the literature it was reported more often that CO₂ activation occurs in the presence of hydrogen near the active metal site. Moreover, hydrogen present near the metal site continuously reduces the metal site oxidized due to CO₂ adsorption, thus regenerating the active site[71].

1.6 Catalyst development through tuning of active sites on GNS / CNF support

Graphene nanosheets (GNS) and carbon nanofiber (CNF) support was utilized for CH₄ assisted and CH₄ – CO₂ assisted biomass reforming. When the catalyst support was changed from zeolite (ZSM-5) to GNS / CNF, molybdenum (Mo) was synthesized as β-Mo₂C naturally during the pyrolysis process. β-Mo₂C was instrumental active center for hydrodeoxygenation (HDO) reforming in biomass oxygenates. However, without transition metal dopant in β-Mo₂C, the reforming reaction is not effective as two different active sites are required for methane activation and HDO reforming. Novel catalyst development performed for synergistic biomass reforming process consists of Fe / Fe₃C – Mo₂C nanoparticles dispersed in intricate carbon nanofiber / nanowire mesh obtained by pyrolysis of hardwood biomass used as feedstock. Iron (Fe) was present in metallic form for the first 2 to 3 cycles and later formed a mix of Fe – Fe₃C active sites in varying ratios depending on the loading percentage, reaction temperature, and number of cycles performed. Addition of a transition metal on the β-Mo₂C crystal structure significantly improves the reforming reactions as it provides distinctly different active sites for CH₄, CO₂ activation which

frees Mo₂C active sites for further biomass reforming. DFT calculations for dual active center catalyst system showed that addition of transition metal such as Fe, Ni, Pd lowers the barrier for desorption of products in gas phase significantly. H₂ and CO are less stable on the Fe / Fe₃C doped β -Mo₂C nanoclusters compared to the homogeneous β -Mo₂C active sites. For example, on Fe-a-Mo₂C – CNF, desorption barrier for H₂ was 1.15 eV compared to 1.70 eV on Mo₂C-CNF. Lowering of desorption barrier was more pronounced in the case of CO. Desorption barrier for CO was just 2.87 eV on Fe-a-Mo₂C-CNF compared to 3.67 eV on Mo₂C-CNF. Catalyst regeneration was achieved with tuning of Fe / Fe₃C active sites. With lower loading dispersion of Fe (0.5% to 2.5%) along with 4% Mo₂C impregnated on biomass, pyrolysis at 700°C yielded Fe, β -Mo₂C active sites on graphene nanosheets (GNS) support. However, with Fe loading concentration of 5 wt.%, synthesized catalyst support was carbon nanofibers (CNF) and carbon nanotubes (CNTs). It was observed that, subjecting the catalyst to multiple reaction cycles (up to 15), Fe active sites immediately converted to Fe₃C and Fe₃C_x after being saturated with neighborhood carbon. Interestingly, between 2nd and 15th cycle, nucleation of carbon chain growth occurred on the Fe₃C_x sites which lead to CNF / CNT growth on the GNS supported catalyst and GNS growth on the CNF / CNT supported catalyst. Graphene nanosheet (GNS) growth was observed in multiple reaction cycles on the 5% Fe-4% Mo₂C – CNF catalyst in reaction temperature range of 800°C to 900°C. This self-regeneration mechanism is explained in detail in the discussion section.

1.7 Experimental and DFT integrated approach to methane assisted biomass reforming

Density functional theory (DFT) calculations and micro-kinetic modelling was performed over TM-doped-Mo₂C surface to study CH₄ activation and reactivity of p-cresol on a metal – metal carbide catalyst. TM replaced Mo₂C and TM added Mo₂C scenario were compared with pure Mo₂C to identify bifunctionality of the catalyst in methane assisted p-cresol reforming reaction. CH₄ activation is thought to occur on TM active sites while oxygenated functional groups in biomass viz. C-OH, C=O, COOH are selectively adsorbed on oxophilic Mo₂C active sites. Monometallic catalyst and bimetallic catalyst were synthesized for reforming of a model compound viz. p-cresol for developing a bottom-up approach in studying the reaction mechanism of methane assisted biomass reforming. P-cresol contains phenolic and methyl functional moieties similar to that in ligno-cellulosic biomass. P-cresol and m-cresol have been widely used to study hydrodeoxygenation elsewhere.[72–75] Proposed reaction mechanism is based on

hydrodeoxygenation and SMR. Thus p-cresol is an ideal model compound for studying selective adsorption of -OH and -CH₃ on active catalytic sites[76]. In the present study, attempts were made to understand role of bifunctional transition metal catalyst for methane activation as a source of H₂ and sequential HDO of p-cresol. Scaling up from p-cresol to lignin and biomass was done based on the O:C ratio. Higher the oxygen content, better is the degree of reforming through HDO and ring opening. O:C weight ratio in three feedstocks is as follows: p-cresol (0.19) < lignin (0.46) < biomass (1.09) thus making p-cresol a good starting point to study the reaction mechanism of simultaneous HDO and methane activation. Catalyst evaluation and screening was performed using transition metals (TM) viz. Fe, Ni, Mo, and Pd on a synthesized graphene nanosheets (GNS) support. TM doped Mo₂C nanoparticles supported on GNS act as dual active centers in the biomass reforming reaction.

1.8 Process scale-up to bench scale Bubbling Fluidized Bed Gasifier (BFBG)

Flare gas assisted biomass reforming approach is being scaled up to a bench-scale fluidized bed gasifier from lab scale fixed bed system to study scalability and reaction engineering in a 1.5 inch (38.1 mm) ID reactor almost 3 times the diameter of tubular fixed bed reactor (ID: 12.7 mm). Moreover, fluidization hydrodynamics and reaction environment is vastly different to that of the fixed bed reactor. In fast fluidization regime, a BFBG reactor is close to continuously stirred tank (CSTR) ideal reactor compared to fixed bed which in ideal operation is a plug flow reactor (PFR). Of particular interest for this project, the high-temperature BFBG operation (800°C to 1000°C) provides a good insight into the fluidization hydrodynamics of the bed-fuel binary mixture and the complex gasification chemistry. For example, the literature suggests that fast fluidization typically occurs between two to five times the minimum fluidization (U_{mf}), but the range is large when energy efficiency considerations are made. Moreover, from a chemistry perspective, the BFBG efficiency correlates with the rapid and uniform mixing of the feedstock and bed, with the reactor operating ideally as a continuously-stirred tank reactor (CSTR)[77,78,87,79–86]. Development of bench-scale fluidized bed gasifier began with cold flow test rig development of 1:1 scale compared to the high temperature fluidized bed reactor. A 1.5-inch diameter cold flow rig with variable bed height was extensively tested for binary mixture of biomass and sand, glass beads as bed media. Bed aspect ratio (ratio of static bed height to bed diameter) was varied using 100 g, 200 g, and 300 g binary mixtures of hardwood biomass particles and bed material. Cold flow rig was used for high speed imaging of the fluidization behavior in biomass binary mixtures at ambient conditions,

pressure drop across the distribution plate and bed, while observing the minimum fluidization velocity, influence of bed particles size and sphericity distribution, and bed aspect ratio.

A schematic for modular shale gas assisted biomass reforming to hydrogen rich syngas in a fluidized bed reactor system is shown in Figure 2.

Figure 2 Process schematic of modular shale gas - biomass co-processing concept

1.9 Co-gasification of biomass, Coal, and waste Plastics

Biomass thermochemical conversion to syngas for fuels and value-added chemicals is an alternative sustainable approach for reducing overall green-house gas emissions[88]. Combined with post-gasification / combustion capture of CO₂, SO₂, and NO_x, thermochemical conversion of waste biomass in the form of forest residues, switchgrass, or lignin can produce carbon-neutral syngas and chemicals. However, high oxygen content of biomass usually leads to poor quality of syngas for applications in downstream chemical / fuel synthesis. Low hydrogen content of biomass

and low calorific value are some of the other challenges of converting biomass to syngas[89]. Solution to increase the overall energy density, calorific content, and H/C ratio lies in mixing the biomass with medium to high rank coal (abundant resource in the US) and with waste plastics[90]. Catalytic gasification of solid feedstock has been shown to enhance the conversion, reaction rates, and promote reforming reactions over coke formation and methanation reactions. For example, Alvarez et al. observed a significant improvement in gas yield (57 wt%) and H₂ concentration (36 vol%) when 20 wt% of plastic wastes was mixed with wood sawdust the biomass in the presence of a Ni/Al₂O₃ catalyst.[91] With retrofit amine based or sorbent based technologies already commercialized for more than 90% CO₂ capture pre- or post-combustion, just 20 to 30 wt.% biomass is required to achieve zero net carbon emissions. Moreover advantages of co-gasifying multiple waste solid feedstock like biomass and plastics, sustainable process development could be achieved to transition from heavily fossil-dependent energy to renewable energy. This can also address other issues such as bio-waste management and reduction in green-house gas emissions. Non-recyclable plastics from Municipal Solid Waste (MSW) can also be used as feed through this technique[91]. However, several limitations such as limited understanding of the reaction chemistry of co-gasification pose significant challenge in developing accurate models for high complexity high-temperature multi-phase process. Current state-of-the-art large scale gasification technologies are based on the understanding of detailed reaction chemistry of either coal or torrefied biomass feed. However, plastic waste is highly variable in composition and non-homogeneous as compared to coal and biomass. Moreover, plastics waste gasification can release toxic emissions particularly the waste with high chloride content. Secondly, plastic waste when exposed to heat liquifies and can form agglomerates with the bed material in fluidized bed reactor causing operational problems and poor fluidization hydrodynamics[92,93]. It has been suggested that increasing the weight of bed materials and temperature can reduce agglomerate formation but detailed investigation is needed for correlating the changes in fluidizing gas velocity or bed height. Therefore new models specifically developed for efficient co-gasification of multiple feeds are needed to address both waste management and GHG emission issues. More research is yet to be performed for studying the effects of coal / biomass / plastics ratio on syngas composition, non-homogeneity of plastics feed, feedstock mixing effects on the reaction kinetics of gasification, optimum gasification temperature, suitable catalyst for such reaction system. Exploratory research

has been performed using lab scale tubular fixed bed reactor system to study the optimum ratio of coal-biomass-waste plastics for gasification to syngas with less CO₂ concentration.

Chapter 2: Methods Section

2.1 Reactor Configurations

2.1.1 Fixed bed reactor setup – reaction conditions

Catalytic hardwood-pellet biomass gasification was performed in a downdraft fixed bed reactor (12.7 mm diameter, 915 mm long) stainless steel (316SS) reactor tube (Charleston Valve and Fitting Co.). In a typical experimental test, 0.75 g of Mo-Fe/ZSM-5 catalyst was premixed with 1g lignocellulose hardwood-pellet biomass. Elemental composition of the biomass is shown in Table 1. Biomass was ground and screened to a mean particle diameter of 432 microns. A Carbolite furnace was used for the high temperature reaction using a programmable controller. Initially, the fixed bed reactor tube is filled completely up to 50 psig with a mixture of 10 sccm methane, 2 sccm carbon dioxide (for $\text{CH}_4 - \text{CO}_2$ assisted biomass reforming), and 188 sccm nitrogen. The bed temperature was raised to the desired reaction temperature with a heating rate of $10^\circ\text{C min}^{-1}$ and held for 60 minutes. The reactor valves at the top and bottom were closed when the tubular reactor was saturated with feed gas. The pressure at which the feed gas in the reactor reached its maximum volumetric capacity was adjusted to be 50 psig. Thus the total gas mixture in the in the tubular reactor at start ($t = 0$) was 0.0695 moles. Mole% of CO_2 and CH_4 was 1 and 5 respectively. Weight% of CO_2 and CH_4 w.r.t biomass on dry basis was 3.06 and 5.56 respectively. Once the reactor bed is filled up to the required pressure, the temperature ramp was started at $10^\circ\text{C min}^{-1}$. Depending on the reaction temperature, the reactor pressure was around 250 psig for 750°C , 380 psig at 850°C , and 420 psig at 900°C . Fixed bed reactor setup is shown in Figure 3. Table 1 shows the elemental composition and proximate analysis of the solid feedstock used in the $\text{CH}_4 / \text{CH}_4 - \text{CO}_2$ assisted reforming reactions. Table 2 shows the experimental conditions and operating parameters along with catalysts used for the reforming studies.

Table 1 Elemental composition and proximate analysis (hardwood biomass) performed by National Research Center for Coal and Energy (NRCCE) for WVU. Alkali lignin and p-cresol were obtained from Sigma Aldrich.

	Carbon (C)	Hydrogen (H)	Oxygen (O)	Moisture	Ash
Hardwood biomass	45.25	4.65	49.2	7.16	0.32
Alkali lignin (C ₆₇ H ₇₁ O ₂₃)	64.68	5.71	29.61	-	-
p-cresol (C ₇ H ₈ O)	77.77	7.4	14.81	-	-

Table 2 Experimental conditions for reforming studies performed in the tubular fixed bed reactor system

Parameters	CH₄ assisted biomass reforming	CH₄ – CO₂ assisted biomass reforming	CH₄ – CO₂ assisted cyclic biomass reforming with in-situ regeneration	CH₄ assisted reforming (Experimental & DFT studies)	CH₄ / C₂H₆ / Eagle Ford shale assisted biomass reforming	Biomass, coal, and waste plastics co-gasification – catalytic & non-catalytic
Temperature (°C)	850, 950	750, 850, 950	800, 850, 900	800	800, 850	800
Reactive Gas Feed %-mol.%, balance N₂	5 to 15% CH ₄	5% CH ₄ 1% CO ₂	5% CH ₄ 1% CO ₂	5% CH ₄	5% CH ₄ or 5% C ₂ H ₆ or Eagle Ford shale	No reactive gas or gasifying agent, pure N ₂
Solid feedstock	Hardwood biomass	Hardwood biomass	Hardwood biomass	p-cresol, alkali lignin, hardwood biomass	Hardwood biomass	Southern pine biomass, Illinois #6 coal, plastics
Flow rate	10 sccm CH ₄ 190 sccm N ₂	10 sccm CH ₄ 2 sccm CO ₂ 190 sccm N ₂	10 sccm CH ₄ 2 sccm CO ₂ 190 sccm N ₂	10 sccm CH ₄ 190 sccm N ₂	10 sccm CH ₄ / 10 sccm C ₂ H ₆ 190 sccm N ₂	200 sccm N ₂
Catalyst	0.5% Fe with 4% Mo on ZSM-5 support	0.5% Fe with 4% Mo ₂ C on CNF support	0.5% / 2.5% / 5% Fe with 4% Mo ₂ C on GNS / CNF support	0.5% Fe / Ni / Pd with 4% Mo ₂ C 2% Fe / Ni & 4% Mo ₂ C on GNS support	0.5% / 2.5% / 5% Fe with 4% Mo ₂ C on GNS / CNF support	0.5% Fe-4% Mo ₂ C-GNS, 5% Fe-4% Mo ₂ C-CNF FeOOH-SO ₄
Reaction pressure psig, (MPa)	380 to 450 (2.6 to 3.1)	250 to 420 (1.7 to 2.9)	220 to 250 (1.5 to 1.7)	100 to 120 (0.69 to 0.83)	400 (2.75)	300 (2)

Figure 3 Schematic of the fixed bed reactor setup for flare gas / CO₂ assisted biomass reforming

2.1.2 Bubbling fluidized bed gasifier

Figure 4 shows the BFBG test stand. The main components are the high-temperature furnace, the BFBG reactor, the double-screw feeders for feedstock delivery, and the micro gas chromatograph (Inficon Fusion) for real-time product composition measurements as shown in Figure 4(a). The high temperatures (up to 1500°C) top-loading furnace (Lucifer Furnaces Inc.) shown in Figure 4(a, c) has an internal diameter of 6 inches, which, with a suitable design, can accommodate up to a 6 in OD reactor. The control unit of the furnace can separately adjust the set point temperature and ramping rate of three different furnace sections (bottom, middle, and top). The maximum temperature reached at the bottom, middle, and top furnace sections during the experiments were 850°C, 1000°C and 1000°C, respectively.

With respect to its design, the BFBG reactor was made of Inconel (an oxidative-corrosion resistant metal alloy), which is typically used in high temperature applications (see Figure 4(c)). Its dimensions are identical to that of the cold flow rig. The BFBG consists of a plenum below the distributor plate, the distributor plate section, the bed reactor, the transition cone, and the disengagement zone (freeboard), which also contains the connections for the feeding line, product gas, and various temperature and pressure sensors. Several filters (Swagelok, 0.5-micron, SS 316) were placed in the product gas and pressure transducer lines to prevent particle entrainment to the

sensitive analysis instruments and sensors. The initial feedstock (coal and biomass) feeding line was a downdraft feeding line that used nitrogen under pressure as a carrier gas. The feedstock comes vertically to the freeboard cap then flows directly on top of the bed material using a guiding tube welded below the freeboard cap. A 100-micron grade mesh welded at the freeboard cap does the primary filtering of the product gas, which then cools down in two expansion tanks. The remaining particles and tar are collected below the expansion tank using the gravitational force as shown in Figure 4(c). The product gas is filtered again with a 2-micron gas filter before being delivered to the GC for product analysis. Table 3 describes the experimental conditions for biomass and coal gasification performed as part of preliminary tests on the BFBG.

Table 3 Experimental conditions of preliminary and planned tests on BFBG test stand

Parameters	Hardwood biomass	Pittsburgh #8 coal	CH₄-CO₂ assisted biomass reforming (planned)
Temperature	900°C	900°C	800°C, 850°C, 900°C
Gasifying / reforming agent	None	10 mol.% Steam	5 mol.% CH ₄ / 1 mol.% CO ₂
Fuel capacity	1 to 2 g min ⁻¹	2 g min ⁻¹	4 to 12 g per test
Flow rate	8 SLM	8 SLM	8 SLM
Catalyst	None	None	Fe-Mo ₂ C-CNF

Table 4 shows the LHV values for syngas components viz. CO, H₂, and CH₄ along with approximate LHV values for syngas obtained in preliminary gasification tests on biomass and coal.

Table 5 shows elemental and proximate analysis of the hardwood biomass, Pittsburgh #8 bituminous coal performed by National Research Center for Coal and Energy (NRCCE) at WVU.

Table 4 LHV values of CO, H₂, CH₄, and syngas from biomass and coal

	CO	H ₂	CH ₄	Syngas (biomass)	Syngas (coal)
LHV (MJ Nm ⁻³)	12.62	10.78	35.82	11.36	11.72

Table 5 Elemental and proximate analysis of biomass and coal wt.% dry basis

	Carbon (C)	Hydrogen (H)	Oxygen (O)	Sulfur (S)	Ash
Biomass, lignin, and model compound (p-cresol) composition					
Hardwood biomass	45.25	4.65	49.2	0.01	0.32
Southern Pine biomass	53.88	5.33	39.25	0.04	1.09
Alkali lignin	64.68	5.71	29.6	-	-
p-cresol	77.78	3.70	14.81	-	-
Coal composition					
Pittsburgh #8 coal	73.62	4.38	7.83	2.51	7.89
Illinois #6 coal	71.72	5.06	7.75	2.82	10.91
Eagle Ford shale Composition (mole %)					
Feed	C1 (CH ₄)	C2 (C ₂ H ₆)	C3	C4	CO ₂
Eagle Ford	66.6	16.3	8.5	6.5	2.0

Figure 4 Bubbling fluidized bed gasifier test stand designed and constructed at WVU

2.2 Catalyst preparation

2.2.1 TM-Mo₂C / CNF / GNS catalyst synthesis:

A carbon nanofiber catalyst impregnated with iron (Fe) and molybdenum (Mo) was utilized in all the experimental tests performed for bi-reforming in synergistic methane activated biomass gasification. The idea of a carbon nanofiber (CNF) catalyst was originated from the study presented by Xie et al on in-situ tar reformation during biomass gasification using iron (Fe), nickel (Ni) impregnated on CNF. For example, about 10g hardwood pellet biomass particles ground and screened to a mean particle size of 300 microns were used as starting material for preparation. 400 ml solution containing 0.01 M Fe³⁺ and 0.01 M Mo⁶⁺ were obtained from iron (III) nitrate nonahydrate and ammonium molybdate (VI) tetrahydrate salts respectively. The 400 mL solutions were mixed with biomass particles and stirred for about 6 hours using a Fischer Scientific hot plate and magnetic stir needle. The solution was allowed to dry for about 24 hours at 105°C. Dried wood chips impregnated with Fe and Mo were pyrolyzed using a tubular fixed bed reactor at 700°C with a 200 sccm flowrate of nitrogen (N₂). The pyrolysis of metal impregnated biomass leads to devolatilization of biomass to CH₄ and other gaseous products like H₂, CO, and CO₂. Molybdenum which was typically 4 wt.% was converted completely to β-Mo₂C. Other transition metals like Fe and Ni lead to crystalline carbon growth during pyrolysis synthesis. Depending on the Fe loading concentration (0.5 wt.% to 5 wt.%), lower Fe loading catalysts are synthesized with graphene nanosheets as the support whereas 5 wt.% Fe catalyst lead to extensive growth of carbon nanofibers and carbon nanotubes. Thermal cracking of biomass and devolatilization lead to deposition of carbon from devolatilized methane (CH₄).

2.2.2 Fe-Mo / ZSM-5 catalyst synthesis:

Zeolite based catalyst (Zeolyst, Inc.) was NH₄ – ZSM-5 with a silica/alumina (SAR) of 23. Ammonium molybdate (VI) tetrahydrate and iron (III) nitrate nonahydrate were purchased from Acros Organics. The zeolite catalyst was first calcined at 500°C in air for 3 h to convert NH₄ – ZSM-5 to H – ZSM-5. The conventional incipient wetness technique was used to prepare Mo-Fe/ZSM-5. After drying the catalysts at 105°C to remove the water overnight, the dry powder catalyst sample was further calcined in air at 550°C for 4 h. The chemical compositions of the synthesized catalysts are shown Table 6.

Table 6 Catalyst compositions used for four different investigations of CH₄ / CH₄-CO₂ assisted biomass reforming

Biomass reforming investigations	Catalyst (‘%’ is weight %)		Support
CH ₄ assisted hardwood biomass reforming	0.5% Fe – 4% Mo		ZSM-5
CH ₄ – CO ₂ assisted biomass reforming	0.5% Fe – 4% Mo		ZSM-5
	0.5% Fe – 4% Mo ₂ C		CNF
In-situ self-regeneration of catalyst through CH ₄ – CO ₂ assisted cyclic biomass reforming	0.5% Fe	4% Mo ₂ C	GNS
	2.5% Fe		GNS / CNF
	5% Fe		CNF
Experimental – DFT integrated investigation of CH ₄ assisted reforming of p-cresol / lignin / biomass	2% Fe		Graphene nanosheets (GNS)
	2% Ni		
	4% Mo ₂ C		
	0.5% Fe	4% Mo ₂ C	
	0.5% Ni		
	0.5% Pd		
Ethane / Eagle Ford shale assisted biomass reforming	0.5% Fe	4% Mo ₂ C	GNS
	2.5% Fe		GNS / CNF
	5% Fe		CNF
Biomass + coal & Biomass + coal + waste plastics co-gasification	0.5% Fe	4% Mo ₂ C	GNS
	5% Fe		CNF
	FeOOH-SO ₄		No support

2.3 Product analysis

Inficon Fusion micro-GC used for product analysis consisted of a molecular sieve column for detection and quantification of H₂, N₂, CH₄, and CO along with a Plot U column for CO₂, ethane, ethylene, and acetylene. Ultra-high purity (UHP) gases from Airgas were used for GC calibration.

In some cases when the product line was directly connected to the gas chromatograph, product gases were collected in sampling bags Tedler (SKC) from the fixed bed reactor or BFBG reactor.

2.4 Catalyst characterization

2.4.1 Scanning electron microscopy (SEM)

A Hitachi Scanning Electron Microscope (SEM) S-4700 was employed for imaging of fresh and spent catalysts at with a voltage of 5 to 15.0 kV at a working distance around 12.0 mm with the electron current between 10 μ A to 18 μ A.

Applications:

- SEM imaging of fresh and spent Fe-Mo / ZSM-5 and Fe-Mo₂C-CNF catalysts for CH₄ – CO₂ assisted biomass reforming[31]
- SEM imaging and Energy Dispersive X-Ray (EDX) mapping of fresh Fe-Mo₂C-GNS and Ni-Mo₂C-GNS catalysts[94]

2.4.2 Thermogravimetry Analysis (TGA)

Measurements were performed on in-house TA instruments' – Waters LLC SDT 650 for oxidation of CNF supported catalysts. Measurements were recorded as weight% of the sample and heat flow in the TGA reactor over temperature range of ambient to 850°C in 2 vol.% O₂ – 98% He atmosphere. Figure 32, Figure 64, Figure 65, Figure 66, Figure 67 show weight% (*y1-axis*), heat flow (W/g, *y2-axis*) vs. temperature (°C, *x-axis*) for 0.5Fe and 2.5Fe (combined), 800-5Fe, 850-5Fe, and 900-5Fe catalyst cycles respectively. TGA results are discussed in the self-regeneration mechanism section of this article.

2.4.3 X-Ray Diffractometry (XRD)

PANalytical X'Pert Pro Diffractometer from West Virginia University's Shared Research Facilities (SRF) was used for measurements on catalyst samples. Cu K α radiation was used for all measurements at 40 kV and 40 mA.

Applications:

- XRD of fresh and spent Fe-Mo₂C-CNF catalyst samples from CH₄ – CO₂ activated biomass reforming[31]
- XRD of fresh and spent Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalyst samples from CH₄ assisted reforming of lignin[94]

- XRD of 0.5Fe, 2.5Fe, 5Fe catalyst samples from in-situ self-regeneration of Fe / Fe₃C – Mo₂C – CNF over 15 cycles.[95]

2.4.4 Transmission Electron Microscopy (TEM)

Jeol JEM-2100 TEM was used for imaging the Fe-Mo₂C-CNF catalyst samples over increasing cycles at different experimental conditions. Imaging was performed at 200 kV with beam current of ~110 μ A. Gatan ES500W camera was used for imaging with magnification ranging from 200Kx (100 nm) to 600Kx (20 nm).

Applications:

- TEM of Fe-Mo / ZSM-5 and Fe-Mo₂C-CNF catalyst samples from CH₄ – CO₂ activated biomass reforming[96]
- TEM of fresh and spent Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalyst samples from CH₄ assisted reforming of lignin[94]
- TEM of 0.5Fe, 2.5Fe, 5Fe catalyst samples from in-situ self-regeneration of Fe / Fe₃C – Mo₂C – CNF over 15 cycles.[95]

2.4.5 Raman Spectroscopy

Renishaw InVia Raman microscope from SRF was utilized for measurements for d-peak and g-peak on Fe-Mo₂C-CNF samples to study changing quality of CNF supported catalysts over increasing number of cycles. Green laser with excitation wavelength of 532 nm with 5% power (5 mW). Three scans were accumulated and averaged for each measurement.

Applications:

- Raman spectra of fresh and spent Fe-Mo₂C-GNS and Ni-Mo₂C-GNS catalyst samples from CH₄ assisted reforming of p-cresol.[94]
- Raman spectra of 0.5Fe, 2.5Fe, 5Fe catalyst samples from in-situ self-regeneration of Fe / Fe₃C – Mo₂C – CNF over 15 cycles.[95]

2.4.6 XPS Spectroscopy

Physical Electronics PHI 5000 VersaProbe XPS instrument was used for obtaining spectral scans of the Fe-Mo₂C-GNS and Ni-Mo₂C-GNS catalysts. Survey scan and detailed scans were obtained for C-1s, Mo-3d spectra. Peak analysis and fit was performed using Gaussian function and algorithm in OriginLab 2020.

2.5 Conversion definitions & overall yields

- **Hydrodeoxygenation-Hydrogenolysis conversion.....Equation (1)**

$$\text{HDO conv} = \frac{\text{Moles of O in CO, CO}_2 \text{ product gas} - \text{Moles of O in CO}_2}{\text{Starting Moles of O in solid feedstock}} \times 100$$

- **Hydrogen conversion.....Equation (2)**

$$\text{H}_2 \text{ conv} = \frac{\text{Moles of H in H}_2 \text{ product gas} - \text{Moles of H from CH}_4}{\text{Starting Moles of H}_2 \text{ in solid feedstock}} \times 100$$

- **Carbon conversion.....Equation (3)**

$$\text{C conv} = \frac{\text{Moles of C in CO, CH}_4, \text{ CO}_2 \text{ product gas} - \text{Moles of C from CH}_4, \text{ CO}_2}{\text{Starting Moles of O in solid feedstock}} \times 100$$

- **Gas yield.....Equation (4)**

$$\text{Gas yield} = \frac{\text{wt. of reactant converted to syngas}}{\text{wt. of solid reacting feed on dry basis}} \times 100$$

- **Tar yield = amount of heavy aromatics trapped in methanol solvent.....Equation (5)**

- **Coke = (% weight loss from TGA oxidation of spent catalysts) × (amount of residue after reaction).....Equation (6)**

2.6 DFT methodology

To understand the relative activity of the bifunctional transition metal doped Mo₂C catalyst in methane assisted p-cresol reforming reaction, adsorption energies of reactant, intermediates and product species were studied using density functional theory (DFT). Geometry optimizations were performed using plane wave DFT code as implemented in Vienna ab initio simulation package (VASP-5.4.4 version)[97]. The core-electrons of the system were represented using Vanderbilt Ultra-soft pseudopotentials (USPP)[98], whereas valence state electrons were expanded using plane wave basis function. The plane-wave basis functions were truncated at a cut-off energy of 396 eV. Revised Perdew-Burke-Ernzerhof (RPBE) exchange correlation functional developed by Hammer et al.[99,100] was used.

The Mo₂C (001) surface was modeled using a four-layer surface slab of size 4x4, as has been used by Medford et al[101,102]. To study the bifunctional transition metal doped Mo₂C catalyst, 3 different models were employed, as shown in Figure 5. In model Figure 5(b), one Mo atom from the surface was replaced by transition metal (TM-r-Mo₂C); whereas in Figure 5(c) single transition metal atom was added to the Mo₂C(001) surface (TM-a-Mo₂C). The surface slabs were periodically repeated with 20 Å vacuum along the z-axis. During the geometry optimization the

bottom two layers of the Mo_2C are fixed while the upper half along the adsorbate were allowed to relax. Convergence criteria for force and energy are set to $0.05 \text{ eV/\AA}$ and 10^{-6} eV , respectively. Monkhorst-Pack k-point sampling of $2 \times 2 \times 1$ along with Gaussian smearing parameter of value 0.02 were used for all the calculations.[103] All the calculations were performed under spin-polarized condition.

To understand the catalytic activity of Ni-strip over Mo_2C surface, the Ni- strip-add- Mo_2C surface was modeled by adding a strip of Ni layer over the $\text{Mo}_2\text{C}(001)$ surface, as shown in Figure 6(a). Similarly a Ni(111) surface was obtained by cleaving the Ni-FCC crystal in the (111) direction (Figure 6(b))

Figure 5 DFT optimized geometry of pure and transition metal doped Mo_2C surfaces. (a) $\text{Mo}_2\text{C}(001)$ surface; (b) $\text{Mo}_2\text{C}(001)$ surface with one surface Mo atom replaced by transition metal; (c) $\text{Mo}_2\text{C}(001)$ surface with one transition metal ad-atom at the surface. Transition metals studied were Fe and Ni.

Figure 6 DFT optimized geometry of (a) Ni-strip-add-Mo₂C surface; (b) Ni(111) surface. Transition metals studied were Fe and Ni. Color code: Mo (turquoise), Ni (blue), C (black), H (white).

Chapter 3: Proof of Concept and Proposed Reaction Pathway for Methane & Methane – Carbon Dioxide Assisted Biomass Reforming

Methane assisted biomass reforming and methane-carbon dioxide assisted biomass reforming was performed to demonstrate proof-of-concept investigation of shale gas-biomass co-processing theory. Methane (which constitutes anywhere between 50 to 70 mol.% of the shale gas) was selected for the proof-of-concept investigation to determine the optimum reacting conditions and most-probable reaction pathway of the methane assisted biomass reforming. Ligno-cellulosic biomass rich in oxygen (comparable to carbon by wt.%) has to be reformed through complex reactions sequences like hydrodeoxygenation (HDO) and hydrogenolysis. Pure hydrogen feed is generally used for such kind of reforming over expensive metal supported catalysts like Pt added Ni-CeO₂-Al₂O₃, Ni-MCM-41, Pt/Fe/Co promoted Ni-dolomite, MoAg / MoZn on ZSM-5. This study investigates the performance of methane driven HDO and hydrogenolysis reforming of biomass over conventional Fe-Mo / ZSM-5 catalyst and innovatively synthesized Fe-Mo₂C nanoparticle dispersed carbon nanofiber (CNF) supported catalyst. Here methane is primarily used as an indirect hydrogen transfer source for oxygen removal from complex biomass oxygenates mainly characterized as interconnected phenolic groups. CH₄ contains high H to C_{eff} ratio of 4 while ethane (C₂H₆) has H to C_{eff} ratio of 3. Section 3.1 discusses the experimental results and proposed reaction pathway in methane activated catalytic biomass gasification to hydrogen rich syngas.

Section 3.2 illustrates in detail the effects of adding 1 mol.% CO₂ with an optimized 5 mol.% CH₄ to the reaction feed with biomass. Based on the results obtained in Section 3.1, it was observed that syngas composition and H₂:CO ratio could be controlled with higher CO production by addition of external CO₂ to the reacting feed. CO₂ addition and catalytic activation over Fe, Mo, and Mo₂C sites at high temperature leads to dry reforming of C₁, C₂, cyclic C_n components from ligno-cellulosic biomass to produce equimolar H₂, CO. High H₂:CO ratio (4 to 10) observed in the CH₄ assisted biomass reforming can be controlled between 2 and 3 with addition of external CO₂. CO₂:CH₄ ratio was maintained at 1:5 to avoid increasing the CO_x products in the resulting syngas and maintain the H₂:CO ratio > 2. CO₂ activation is achieved over transition metal active sites like Fe, Ni at high temperatures in presence of activated hydrogen species on the catalyst surface. CO₂ addition introduces second degree of reforming approach along with HDO, hydrogenolysis

reforming. Therefore, CH₄-CO₂ assisted biomass to syngas is achieved through bi-reforming reaction mechanism presented in detail in Section 3.2.

3.1 Hydrogen rich syngas production through synergistic methane activated catalytic biomass gasification

3.1.1 Conventional biomass gasification and devolatilization studies in TGA

The TGA-MS performed the initial biomass gasification screening tests to identify temperature range for hydrogen and carbon monoxide evolution. Figure 7 shows the concentration profile versus time of the four major syngas components obtained from the TGA-mass spectrometry studies. For devolatilization and gasification at 650°C, only 7% H₂ yield was obtained. CO, CO₂ made up most of the gas yield obtained at temperatures less than 300°C with methane evolving beyond 300°C possibly indicating thermal cracking of the array of oxygenated aromatic rings in the lignin structure of biomass.

Figure 7 Biomass gasification (hardwood pellet; heating rate of 20°C/min, then 30 min at 650°C; 100 sccm He flow)

It is interesting to note that as methane started appearing in the gas products, carbon dioxide yield began to fall and only 6% carbon dioxide remained at 515°C. This suggested that the reverse SMR reaction dominated between 335°C to 515°C, where all the hydrogen that was bonded to saturated / unsaturated carbon in biomass reacted with the CO₂ from devolatilization and thermal cracking

forming CO. Higher CO concentrations were detected at higher temperatures as char oxidation reaction kicks in. Hydrogen started to appear as a predominant species in the normalized concentrations obtained from the mass spectrometry ionization signals only after a threshold temperature of about 650°C. Figure 8 and Figure 9 show that between 650°C to 950°C hydrogen and carbon monoxide constituted most of the gas yield. This indicated that at a lower temperature and without an oxidative atmosphere like steam or air, devolatilization and bio-char formation occurred between 200°C to 600°C[104–106] In the TGA tests, the biomass sample size was too small (~20 mg) to trace any tar formation[107]. In the alumina crucible used for the tests only ash residue was observed with the end weight of the tared crucible around ~0.5 mg. The isothermal reaction time at the test temperatures was sufficient to completely gasify bio-char. Char gasification reactions were observed at higher temperatures, evident by the high H₂:CO and CO/CO₂ ratios at temperatures beyond 650°C/700°C. Surprisingly, no methane formation was observed at char gasification temperatures (650 - 950°C) possibly indicating Boudouard reaction (Eq 7), which converted carbon to CO due to its highly endothermic nature:[46]

Similarly, a sharp increase in H₂ and improvement in H₂ / CO ratio may also be due to continuous heat being supplied driving the endothermic gasification reactions forward. Between 650-950°C, methane was not observed in the product probably because of reforming with water or CO₂, which is evidenced by the increase in CO and H₂ concentration shown in Figure 9.

H₂:CO and CO:CO₂ ratios obtained from non-oxidative biomass gasification in the TGA are shown in Table 7.

Figure 8 Biomass gasification (hardwood pellet; heating rate of 20°C/min, then 30 min at 850°C; 100 sccm He flow)

Typically, methane decomposition occurs at temperatures higher than 1000°C in the absence of a catalyst. Due to the presence of mineral materials in biomass, the methane decomposition reaction cannot be ruled out here. The proportion of tar in dry woody biomass ranges between 5 – 12 mg/g (0.5 - 1.2 wt.% on a dry basis) of dry biomass. [108] With only 20 mg of biomass in the TGA tests, possibility of traceable tar formation is very low.[55,109–111] Endothermic equilibrium reactions in the regime of char gasification and homogeneous volatile reactions may have pronounced effects on the H₂:CO and CO/CO₂ ratios.[112]

Table 7 H₂:CO and CO:CO₂ ratio obtained from non-oxidative biomass gasification in the TGA at temperatures between 750-950°C

Temperature (°C)	H ₂ / CO	CO / CO ₂
750	1.87	16.2
850	1.1	N/A
950	1.1	23

Figure 9 Biomass gasification (hardwood pellet; heating rate of 20°C/min, then 30 min at 950°C; 100 sccm He flow)

Figure 10 illustrates a TGA test where biomass was mixed with ZSM-5 and gasified under identical reaction conditions as used in the previous TGA tests. It was observed that the H₂:CO ratio improved significantly at 750 – 800°C. The presence of ZSM-5 may have enabled cracking reactions at higher temperatures. Notably, a high concentration of methane was observed between 450°C to 550°C, indicating hydrogenation of higher aromatics and some aliphatic chains forming CH₄ almost as much as CO at ~400°C. More CO and H₂ was observed as temperature in the reactor increased. This indicated that the presence of a catalyst like zeolite helped to improve the syngas quality with in-situ tar reformation and cracking. The fixed-bed reactor biomass and methane-

biomass gasification had a significantly different reaction environment, heat flux, and heat flux direction than the TGA sample crucible. Fixed bed reactor operated as a downdraft gasifier, whereas gas flow was horizontal in the case of TGA[113]. The interaction between catalyst active sites, char, and gaseous products was different in the case of the fixed bed reactor as compared to the TGA. Having said this, TGA provided a better study of the evolution and profile of possible gasification reactions occurring in a real reactor like the fixed-bed studies presented in following sections.

Figure 10 Biomass gasification on ZSM-5 (hardwood pellet; heating rate of 20°C/min, then 30 min at 950°C; 100 sccm He flow)

3.1.2 Biomass catalytic gasification in the absence of methane in a fixed-bed reactor

Figure 11 shows that in the absence of methane, biomass gasification yields in a fixed-bed reactor were (on average) 55 mole% and 58 mole% methane for the reaction at 850°C and 950°C, respectively. A H₂:CO ratio between 0.5 and 1.0 was obtained, which was roughly in the range of the conventional non-catalytic gasification. However, with almost 55 - 60% methane in the gas yield, and a very low CO₂ yield of 2 – 13 %, the results suggested that the reverse steam methane reformation (SMR) (Equation 2) was dominant at high temperature as both of these reactions were endothermic. Reverse SMR leading to conversion of hydrogen and carbon monoxide into methane

could be due to the presence of acidic active sites on Fe and Mo metals[114]. In the case of biomass gasification on ZSM-5, the methane was 29 mole%, which is more than 3 times of the one seen in typical non-catalytic biomass gasification. The high methane yield in the product was attributed to the thermal cracking of the aromatic array of biomass. Moreover, in the absence of an acidic oxophilic transition metal like Fe or Mo, the oxygenated carbon in the biomass was converted to CO, CO₂, and H₂ which reacted on the surface. Also, without additional methane in the gas feed, the surface was deficient in methane, which favored the formation of methane and water vapor as the adsorbed CO and H₂ underwent reverse SMR at high temperature.

The results suggest a synergy between methane and biomass, which shifted the SMR equilibrium to right and forms hydrogen rich syngas. Detailed discussion on the results of methane – biomass gasification studies are discussed in the next section. Without external methane feed, typical gasification reactions only yield about 1:1 H₂:CO ratio as is the molar ratio of biomass. Biomass and natural gas both being abundant and largely untapped sources of clean and efficient energy can help meet more than 80% of the total energy needs in the US by 2030. Utilization of natural gas with development of new processes will also help revive the Appalachian economy especially that of West Virginia which strategically lies in the Marcellus shale gas basin[115]. Thus, the synergy between biomass and methane has been explored in the following sections.

Figure 11 Biomass gasification in the absence of methane operated in a fixed bed reactor ZSM-5 support and Mo-Fe/ZSM-5 at temperature: 850°C, 950°C

3.1.3 Coke formation and H₂ from CH₄ decomposition

When using 0.5% and 1.5% Fe promoted Mo/ZSM-5 surface, coke formation was observed during co-feeding of biomass and methane. However, in the absence of methane, biomass gasification, coking was not observed on either catalyst. This indicates that some of the methane in the gas feed is decomposed at high temperatures to form coke and produce hydrogen (H₂) due to the presence of Fe active sites on ZSM-5. Stoichiometric amount of hydrogen formed from methane decomposition was accounted for based on coke formed from methane decomposition.[116] The calculation for hydrogen obtained from biomass-methane synergy was calculated in mole% as follows:

$$H_{2(\text{prod})} = H_{2(\text{total})} - H_{2(\text{coke})} \dots\dots\dots \text{Equation (10)}$$

H₂:CO ratios obtained for various concentrations of methane and reaction temperatures were calculated after accounting for hydrogen obtained possibly from methane decomposition. Very little or no tar was recovered from the gas-liquid separator at the bottom of the vertical tubular reactor. However, small concentrations of ethane, ethylene, and acetylene were seen in the product analysis on the micro-GC.

3.1.4 Gas yield, tar formation, and char deposition on catalyst

Overall carbon balance for the methane activated biomass gasification was performed using inert gas and methane moles before the temperature ramp and molar volume occupied by the gas inside the tubular fixed bed reactor based on reaction temperature and pressure. All of the biomass carbon was recovered using TGA studies of spent catalyst for coke and char characterization. The amount of condensed tar was estimated using hexane solvent wash of the reactor tube and condenser. The mole% and yield of individual products was calculated based on gas moles obtained in the product. However, authors chose to present mole% and product yield based on syngas moles as it would be more accurate to do so in this case. This is because there was coke deposition on the catalyst as presented in the manuscript and hydrogen from methane decomposition was not considered as hydrogen produced from methane-biomass synergy. To be consistent with the objective of this work which is to show natural gas – biomass synergy, mole% and yield was calculated on product gas mole basis. In all fairness, if one was to calculate mole% on basis of starting moles of biomass, the mole% of all the species would be less by about 10% to 20% depending on the gas, tar, and char yield.

Yield (mole%) = number of moles of species / total product gas moles.....equation (11)

It was also observed that normalized product gas composition and mole% calculated from yield of individual species based on gas moles were similar and thus were used interchangeably in discussing the results. It was observed that all the experimental tests produced greater than or equal to 80 mole% product gas. Tar mole% ranged between 10 to 15% while char was only about 2 to 8 mole%. Product gas yield from methane activated biomass gasification can be termed as biomass conversion obtained through the reaction. Gas yield, tar, and char composition of the biomass carbon balance is presented in Figure 12. It was observed that product gas yield was 88 mole% for reaction at 950°C and 84 mole% for reaction at 850°C. It was observed that gas yield substantially increased from 37.5 mole% at 750°C (not shown here) to 84 mole% at 850°C and further to 88 mole% at 950°C. However, gas yield decreased slightly from 84 mole% to 80 mole% at 850°C when gas feed methane concentration was increased from 5 to 15 vol.%. Similar trend was also observed at 950°C as gas yield decreased from 88 mole% to 82 mole% when methane concentration was increased from 5 to 15 vol.%. Marginal increase in char yield from 3 mole% to 8 mole% at 850°C and 2 mole% to 7 mole% at 950°C was also observed when methane

concentration was increased from 5 to 15 vol.%. This could be explained based on the catalyst deactivation phenomenon possibly occurring due to high methane coverage on Fe and Mo active sites leading to paucity of sites available for methane-biomass reaction. Moreover, without methane in gas feed, biomass conversion was much higher on the FeMo1 catalyst (87.5% at 850°C and 90% at 950°C) compared to methane activated biomass gasification tests. However, >80 mole% product gas yield is an indication that low methane concentration leads to high methane and biomass conversion due to Fe and Mo being conducive to methane activation and biomass hydrodeoxygenation. Gas yield, char, and tar components in biomass gasification without methane and methane activated biomass gasification on FeMo1 catalyst in Table 8 and Figure 12.

Table 8 Co-Gasification of Biomass and methane gasification over Fe-Mo/ZSM-5; measured amount of coke on catalyst and gas yield for no-methane biomass gasification

Parameters	850°C	950°C
Gas Yield Biomass-no methane (mole%)	87.5	90.1
Coking FeMo1 (mg, % CH₄)	75.6, 5 135, 10 246, 15	68.2, 5 136, 10 204.5, 15
Coking FeMo2 (mg, %CH₄)	51.5, 5 169.2, 10 267.3, 15	NA

Figure 12 Gas, tar, and char yield obtained in biomass gasification without methane and methane activated synergistic catalytic biomass gasification at temperature: 850°C, 950°C and CH₄ gas feed concentration: 0, 5, 10, 15 vol.%

As described in Table 8, coking on the catalyst was between 10 - 30 wt.% of the original weight of catalyst after reduction. Under identical conditions, biomass gasification in the absence of

methane in the gas feed yielded almost no recoverable coke on the FeMo1 catalyst. No weight loss was seen in the catalyst before and after calcination. It can be concluded that coke deposition on both FeMo1 and FeMo2 catalysts was due to methane decomposition when 5 - 15% was used in the gas feed. The amount of coke from each test using methane is shown in Table 8. No considerable coke formation on the catalyst was observed for biomass gasification without methane, indicating that the aromatic components of lignin with branched functional groups like carbonyl carbon (C=O), hydroxyl carbon (C-OH) undergo surface reactions by latching onto the ZSM-5 acidic sites. Most of the oxygen from the biomass possibly reacted on the surface with the available hydrogen to undergo reverse SMR without external methane (Eq 8).

3.1.5 Synergistic methane assisted biomass reforming on Fe-Mo / ZSM-5

Synergistic methane assisted biomass reforming to produce hydrogen rich syngas was initially demonstrated on the traditional Fe-Mo / ZSM-5 catalyst to conceptually ascertain the synergy between methane activation and hydrodeoxygenation of biomass oxygenates. Reactions were performed at 850°C and 950°C (Figure 13(a, b)). Hydrogen was the dominant species in the product gas with hydrogen to carbon monoxide ($H_2:CO$) ratio as high as 7.5 when reaction was performed at 950°C under 5% CH_4 concentration. As the methane concentration is further increased to 10% and 15%, the $H_2:CO$ ratio dropped sharply at 950°C to 3.8 and 3.7 respectively (Figure 13(b)). The same reaction when performed at 850°C for 5%, 10%, and 15% CH_4 in the feed, $H_2:CO$ drops steadily from 6 to 4.2 (Figure 13(a)). In the absence of a catalyst, typical hardwood biomass gasification produced a $H_2:CO$ ratio of 0.3 to 0.5. This sharp increase in hydrogen by adding methane was an interesting aspect of this study, which likely shows the synergy between methane and biomass at high temperatures on ZSM-5 supported Fe, Mo active sites. In absence of external CH_4 in reaction environment, as high as 70 mole% methane was seen in the product gas with hydrogen yield averaging at 17% at 850°C and 950°C. CO, CO_2 yield averaged at 19% and 11% respectively for 850°C (Table 9). Biomass gasification typically yields $H_2:CO$ less than or close to 1.[109] The synergy between methane and biomass reacting together on an active catalyst like FeMo/ZSM-5 was apparent from the multifold increase in the hydrogen yield. The presence of methane in the gas feed suggested an equilibrium shift in some of the typical gasification reactions with steam methane reforming possibly occurring on the active sites of Mo and Fe. Both molybdenum (Mo) and iron (Fe) are known to be moderately oxophilic that is they have a higher binding affinity to oxygen as compared to metals like Zn, Ni, and Cu but lower

oxygen binding affinity as compared to Ti, V, and Sc amongst the transition state or d-block metals. Mo is slightly more oxophilic than Fe (0.6 and 0.4) thus having the capability to activate C-OH, C=O type of bonds abundantly present in the complex array of aromatics in lignin component of the hardwood biomass.[117] Hydrodeoxygenation (HDO) reactions studied on PdZn surfaces have shown that Zn being an oxophilic metal latches the oxygen present in the functional groups thus activating C-OH bonds.[117]

This study was performed to experimentally investigate the possible synergy co-processing flare gas with highly oxygenated biomass like lignin and hardwood ligno-cellulosic biomass. With O:C weight ratio >1 for the hardwood biomass used in this study, oxygenated functional groups are abundantly present in lignin, cellulose, and hemicellulose components. Oxygenated functional moieties like R-OH, R-OCH₃, R-OC₂H₅ could be hydrodeoxygenated through simultaneous CH₄ activation. CH₄ activation occurs with relative ease on the transition metal sites like Fe, Ni. Mo in turn was found to be extremely effective in strongly binding the oxygen in such oxygenates. Dual active sites viz. Fe and Mo participate in synergistic methane activation and HDO to form steam adsorbates on the Mo active sites. Steam adsorbates reform the CH₄ and other unsaturated alkyl groups from biomass to form syngas products rich in hydrogen. Proposed reaction mechanism is presented in detail in the following section. Following section describes a study exploring biomass – flare gas synergistic co-processing in greater detail on Fe-Mo / ZSM-5 and novel Fe-Mo₂C-CNF catalyst.

Figure 13 CH₄ assisted biomass reforming with CH₄ concentration of 5 to 15 vol.% on Fe-Mo / ZSM-5 catalyst at temperature: a) 850°C b) 950°C

Table 9 Statistical analysis for product composition of syngas components for reaction temperatures 850°C, 950°C without CH₄ and with CH₄ concentration 5 to 15 vol.%

Test Conditions	Syngas species	Average	Standard Deviation	Confidence Interval
850°C, No CH₄	H ₂	16.47	0.11	±0.15
	CO	18.63	4.64	±6.43
	CO ₂	10.81	2.51	±3.48
	CH ₄	54.09	7.26	±10.06
950°C, No CH₄	H ₂	16.35	1.26	±1.43
	CO	23.78	8.11	±9.17
	CO ₂	4.60	3.29	±3.73
	CH ₄	55.27	11.93	±13.50
850°C, 5% CH₄	H ₂	72.64	15.33	±21.2
	CO	12.29	2.96	±4.1
	CO ₂	0.90	0.32	±0.45
	CH ₄	0.81	0.29	±0.4
850°C, 10% CH₄	H ₂	81.58	0.78	±0.88
	CO	16.42	0.44	±0.49
	CO ₂	1.05	0.61	±0.69
	CH ₄	0.94	0.55	±0.62
850°C, 15% CH₄	H ₂	68.26	13.28	±18.41
	CO	16.14	0.79	±1.10
	CO ₂	2.77	0.29	±0.40
	CH ₄	2.49	0.26	±0.36
950°C, 5% CH₄	H ₂	74.90	13.98	±19.37
	CO	10.04	1.94	±2.69
	CO ₂	4.73	3.86	±5.35
	CH ₄	4.26	3.48	±4.82
950°C, 10% CH	H ₂	63.30	20.41	±28.29
	CO	16.83	6.64	±9.21
	CO ₂	0.82	0.61	±0.85
	CH ₄	0.74	0.55	±0.76
950°C, 15% CH	H ₂	70.84	1.57	±2.18
	CO	18.93	1.45	±2.00
	CO ₂	2.13	3.01	±4.17
	CH ₄	3.83	0.00	0

3.1.6 Comparison of catalytic and non-catalytic biomass gasification

Figure 14 and Figure 15 compares the product composition and $H_2:CO$ ratios for hardwood biomass gasification without catalyst and external methane, biomass gasification on ZSM-5 catalytic support without methane, and methane activated biomass gasification with 5 vol.% and 10 vol.% CH_4 on FeMo1 and FeMo2 catalysts. Biomass only gasification was performed non-catalytically and on ZSM-5. On FeMo1 and FeMo2 catalysts, biomass-methane experiments were performed with methane concentration 5% and 10%. The $H_2:CO$ ratio on ZSM-5 more than doubled compared to a typical non-catalytic test. This indicated that the presence of acid sites on ZSM-5 along with Fe active sites provide favorable atmosphere for water-gas shift and SMR reactions. This is evident from the decrease in methane concentration and increase in carbon dioxide formation. The addition of Fe and Mo to ZSM-5 leads to the synergistic interaction between methane and biomass to produce hydrogen rich syngas. $H_2:CO$ increases significantly when methane-biomass gasification was performed on FeMo1 and FeMo2 catalyst. With 5% CH_4 in gas feed, an $H_2:CO$ ratio of ~ 7 was obtained on FeMo1 which increased further to 10 on the FeMo2 catalyst. With 10% CH_4 in the feed, $H_2:CO$ ratio is lower than that for 5% CH_4 , 5 for FeMo1 and ~ 8 for FeMo2 catalyst respectively. Lower $H_2:CO$ ratios observed for higher methane concentrations is possibly due to rapid catalyst deactivation due to coke deposition and high temperature. The comparison of catalytic and non-catalytic biomass and methane activated biomass gasification was in tune with the proposed reaction mechanism in Table 11

Table 11.

Figure 14 Hardwood biomass gasification without catalyst and external methane, biomass gasification on ZSM-5 catalytic support without methane, and methane activated biomass gasification with 5 vol.% CH₄ on FeMo1 and FeMo2 catalysts.

Figure 15 Hardwood biomass gasification without catalyst and external methane, biomass gasification on ZSM-5 catalytic support without methane, and methane activated biomass gasification with 10 vol.% CH₄ on FeMo1 and FeMo2 catalysts.

3.1.7 Conclusions

Methane-assisted biomass reforming was investigated on traditional 0.5% Fe – 4% Mo / ZSM-5 catalyst. The results showed a synergy between external methane and ligno-cellulosic biomass that produced hydrogen-rich syngas with more than 80% hydrogen in the gas yield. The high hydrogen production on the Fe-Mo based catalyst was probably due to the oxophilic nature of both iron (Fe) and Molybdenum (Mo), which converted the oxygen in the various functional groups of lignin to steam that reforms the incoming methane and alkylated components in biomass to form more hydrogen. Catalyst surface and active sites on the metals were also favorable to the high-temperature water gas shift reaction (WGSR), as suggested by the multifold increase in the H₂:CO ratio compared to conventional biomass gasification. However, the H₂:CO ratio dropped by more than 50% when the methane concentration increased from 5 – 15 vol.%, possibly due to partial catalyst deactivation on the conventional ZSM-5 support which is not effective in shielding the active sites from harsh reaction media, coking, and poisoning. The synergistic biomass-methane

non-oxidative gasification created a platform flare gas assisted catalytic reforming of biomass to produce hydrogen rich syngas.

3.2 Biomass – flare gas synergistic co-processing in the presence of carbon dioxide for the controlled production of syngas ($H_2:CO \sim 2 - 2.5$)

3.2.1 Methane activated vs. methane – carbon dioxide activated biomass gasification on 0.5% Fe – 4% Mo / ZSM-5

As discussed in the previous section, methane activated biomass gasification produces hydrogen rich gas which has direct application as a potential hydrogen source. With the addition of 1 vol.% CO_2 in the methane-biomass synergistic reaction environments, synthesis gas can be produced with a $H_2:CO$ ratio between 1.5 to 2.4 (Figure 16). The decrease in hydrogen production and balanced syngas composition is probably the result of in-situ bi-reforming in a single stage reactor. Addition of a small amount of carbon dioxide helps convert excess H_2 produced via synergistic steam methane reforming. In the presence of hydrogen adsorbates and atomic hydrogen on the catalyst neighborhood, carbon dioxide undergoes thermal activation to form formates which is converted predominantly to carbon monoxide (CO). This phenomenon is also termed as dry reforming. Note that CO concentration only marginally increased from 14.2% for methane-biomass reaction to 16.3% for the methane-carbon dioxide-biomass reaction. Carbon dioxide conversion to carbon monoxide through dry reforming roughly consumes 2 hydrogen atoms adsorbed in the neighborhood while producing only 1 atomic hydrogen adsorbate. Also, the zeolite support produces less gas yield in general compared to the carbon nanofiber catalyst as elaborated in the next section. Looking closely at the gas composition, methane composition seems to be low compared to carbon dioxide concentration given that the methane feed was 5 vol.% against 1 vol.% carbon dioxide. This indicates that water-gas shift reaction may be occurring independently of CO_2 dry reforming on some of the unoccupied Fe active sites. Although, SMR driven CO_2 dry reforming consumes hydrogen, the water-gas shift reaction may form some hydrogen and consume CO thus keeping the $H_2:CO$ ratio around 2. Adding more carbon dioxide in the gas feed may hinder WGS and even SMR reactions by inertly occupying most of the active sites. It may lead to a decreased $H_2:CO$ ratio or an increased carbon dioxide concentration in the product gas thus defeating the purpose of carbon dioxide addition altogether. The reason behind 5 times less carbon dioxide than methane in the gas feed is to strategically consume only part of the excess hydrogen

to produce synthesis gas ($\text{H}_2:\text{CO} \sim 2$) which otherwise is difficult to obtain from biomass. This way, methane-biomass synergy is kept intact while exploring trilateral synergy between methane, carbon dioxide, and biomass. Figure 16 shows a comparison plot of biomass gasification composition obtained by methane activation versus methane – carbon dioxide activation at 850°C . The catalyst used in this study was 0.5% Fe – 4% Mo / ZSM-5. Note that the $\text{H}_2:\text{CO}$ ratio with methane activated biomass gasification was 5.9 and with methane – carbon dioxide activation, the $\text{H}_2:\text{CO}$ ratio was 1.94.

3.2.2 Effect of catalyst support on methane-carbon dioxide activated biomass gasification

It was observed that, a $\text{H}_2:\text{CO}$ ratio of ~ 2 was obtained at 850°C with both zeolite and carbon nanofiber support as shown in Figure 17. At 750°C , the $\text{H}_2:\text{CO}$ ratio obtained on both the FeMo-ZSM-5 and Fe-Mo₂C-CNF catalyst was similar (1.18 and 0.96 respectively) as shown in Figure 18. However, FeMo catalyst support has a significant effect on overall reaction yield if not so much on the gas composition of syngas species as shown in Figure 17. For example, at 850°C both FeMo-ZSM-5 and Fe-Mo₂C-CNF produced syngas with an identical $\text{H}_2:\text{CO}$ ratio (1.94 vs. 1.97). At a lower reaction temperature of 750°C , the $\text{H}_2:\text{CO}$ ratio in the product gas was lower for Fe-Mo₂C-CNF than the FeMo-ZSM-5 catalyst (0.96 and 1.18 respectively). However, overall gas yield for the ZSM-5 based reaction was significantly low compared to CNF at both 850°C and 750°C . Effect of catalytic support on syngas yield has been investigated in detail in later sections. On average the FeMo-ZSM-5 reaction produced only about 55 millimoles of product gas (H_2 , CO , CH_4 , CO_2) whereas the Fe-Mo₂C-CNF catalyst-based reaction produced 80 millimoles of product gas. The number of moles of product gas obtained through the reaction was calculated on the inert gas basis and reaction pressure at given temperature. It can be conclusively said that for the methane-carbon dioxide-biomass reaction system, the catalyst support has a profound effect on the overall gas yield. Based on higher gas yield of $\text{CH}_4 - \text{CO}_2$ assisted biomass reforming reaction on Fe-Mo₂C-CNF compared to Fe-Mo / ZSM-5, it can be safely assumed that turnover frequency of the reforming reactions was higher per gram of the catalyst on the CNF support than on ZSM-5 support. Fe-Mo₂C-CNF catalyst has been evaluated in detail for activity and time-on-stream testing in the later sections. CNF supported catalysts protect the vital Fe and Mo₂C active sites better through protective encapsulation of sp^2 hybridized graphene / CNF carbon. Unfortunately, no such protection is offered by the traditional ZSM-5 support for the active sites. The active sites are not shielded from harsh reaction media and are rapidly exposed to coking and poisoning of CH_4 / CO .

This would cause lesser overall gas yield and lower turnover frequency thus explaining similar syngas composition but lower absolute concentration of H_2 and CO .

Figure 16 Hardwood biomass gasification: comparison of methane and methane carbon dioxide activated gasification composition at temperature: 850°C; catalyst: 0.5% Fe – 4% Mo / ZSM-5

Figure 17 Hardwood biomass gasification: comparison of syngas composition based on catalyst support zeolite (ZSM-5) and carbon nanofiber (CNF). Temperature: 850°C; reaction environment: 5% CH₄, 1% CO₂, 94% N₂; metal loading: 0.5% Fe, 4% Mo

Figure 18 Hardwood biomass gasification: comparison of syngas composition based on catalyst support zeolite (ZSM-5) and carbon nanofiber (CNF). Temperature: 750°C; reaction environment: 5% CH₄, 1% CO₂, 94% N₂; metal loading: 0.5% Fe, 4% Mo

3.2.3 XRD measurements Fe-Mo / ZSM-5 and Fe-Mo₂C-CNF before and after the reaction

Figure 19 compares the XRD measurements for fresh and spent carbon nanofiber and ZSM-5 supported catalysts. Characteristic peaks for molybdenum carbide (β -Mo₂C) and iron carbide (Fe₃C) were observed in both fresh and spent Fe-Mo₂C-CNF catalyst. Interestingly, molybdenum and iron carbide peaks were not observed on the fresh and spent FeMo-ZSM-5 catalysts. Instead, iron and molybdenum peaks were identified and shown in different symbols on both the fresh and spent FeMo-ZSM-5 catalyst. Although, there could be some metal oxide peaks in the spent FeMo-ZSM-5 catalyst (not identified here), all of the peaks in fresh and spent Fe-Mo₂C-CNF catalyst are that of β -Mo₂C and Fe₃C (~43.7). CNF supported catalyst has uniform metal carbide crystals dispersed in the nanofiber network. Fe₃C peak is almost indistinguishable in XRD scan of fresh

Fe-Mo₂C-CNF catalyst due to low concentration of iron loading. Spent Fe-Mo₂C-CNF XRD scan shows a clear peak at 43.7°. To further explain the carbide peaks on spent Fe-Mo₂C-CNF catalyst in detail, Figure 19 shows XRD scan on the spent Fe-Mo₂C-CNF. Peak at 26.5° possibly indicates graphitic carbon or carbon from nanofiber structures of CNF. Presence of molybdenum carbide (β -Mo₂C) on the spent Fe-Mo₂C-CNF is confirmed by peaks at $2\theta = 34.5^\circ, 38.1^\circ, 39.7^\circ, 52.3^\circ, 61.9^\circ, 69.9^\circ, 75.1^\circ, \text{ and } 76.1^\circ$. Iron carbide (Fe₃C) peaks were also observed at $2\theta = 43.7^\circ$ and 44.7° . Presence of Fe in elemental form cannot be ruled out but peaks for Fe and additional peaks for Fe₃C were probably not observed because of very low loading of Fe (0.5 wt.%) on CNF catalyst. Iron and molybdenum have a high tendency to form carbides. Molybdenum and iron carbide formation is reported elsewhere for similar reaction conditions in catalytic methane decomposition[118,119]. Presence of carbides of Fe and Mo is an important insight for studying different reaction pathways for proposed steam methane reforming and dry reforming reactions in methane – carbon dioxide activated biomass gasification. Moreover, metal carbide formations on the CNF catalyst support alter the binding energies of the gas phase reactants and products. It is observed from preliminary DFT modelling of the CH₄ – CO₂ – biomass reaction that molybdenum carbide binds most of the reactants strongly. However, hydrogen binds relatively weak in the β -Mo₂C crystal. Thus the release of hydrogen is easier on the metal carbides. Metal carbide formation on the carbon nanofiber support probably occurs during catalyst synthesis.

Figure 19 XRD measurements on the fresh and spent Fe-Mo₂C – CNF and FeMo – ZSM-5 catalysts. Molybdenum and iron peaks have been observed for the ZSM-5 supported catalyst while iron carbide (Fe₃C) and molybdenum carbide (β -Mo₂C) peaks were observed in the CNF supported catalyst (symbols explained in the legend).

3.2.4 Transmission Electron Microscopy (TEM) imaging and elemental analysis

TEM imaging and energy dispersive X-ray (EDX) elemental analysis of the spent Fe-Mo₂C-CNF and spent FeMo-ZSM-5 catalysts was performed as shown in Figure 20. Nanofiber structures can be clearly observed in the spent Fe-Mo₂C-CNF catalyst along with metal carbide crystals dispersed in the intricate nanofibers. EDX analysis shows peaks for Fe, Mo, C, and K. Potassium presence in the catalyst support is an interesting observation and possible role of potassium as a promoter must be investigated. Spent FeMo-ZSM-5 also shows good dispersion of metal particles as seen in the TEM image. Elemental analysis of the spent FeMo-ZSM-5 shows Si, Al, Fe, Mo, and C peak (unmarked). The size of metal carbide crystals in the spent Fe-Mo₂C-CNF catalyst is larger

than that of the metal particles in the spent FeMo-ZSM-5 catalyst. Larger size of the crystals on the spent Fe-Mo₂C-CNF catalysts could be attributed to the favorable thermodynamics for carbide formation at the catalyst synthesis temperature of 700°C during pyrolysis. Metal oxide peaks were not detected in the XRD and O peak is not seen in the elemental analysis using EDX. Although FeMo-ZSM-5 was reduced before reaction, reduction is apparently not required for the Fe-Mo₂C-CNF catalyst. Pyrolysis at 700°C of the metal dispersed CNF precursor causes deoxygenation of the catalyst during devolatilization.

Figure 20 Transmission electron microscopy (TEM) images and EDX elemental analysis of the spent Fe-Mo₂C-CNF and FeMo-ZSM-5 catalysts.

3.2.5 Effect of reaction temperature on syngas composition of methane – carbon dioxide activated biomass gasification

Reaction temperature has a profound effect on syngas composition and especially the H₂:CO ratio obtained by methane – carbon dioxide activated biomass gasification. As shown in Figure 21, the H₂:CO ratio is increased from 0.96 at 750°C to 2 at 900°C. There is no significant difference between the H₂:CO ratio at 850°C and 900°C. At 750°C, gas yield from methane-carbon dioxide

activated biomass gasification is only 29.3 mmoles while liquid yield which can be categorized as tar was 54 millimoles. Thus, most of the biomass present in the reactor before the start of the temperature ramp was converted to tar in the form of liquid. At 850°C, the gas yield increased substantially from 29.3 mmoles to 82 mmoles and moles of liquid decreased from 54 millimoles to 10 millimoles.

When the temperature was further increased to 900°C, gas yield increased to 98.5% while the liquid moles decreased to 2 millimoles. Temperature has a significant effect on the gas and tar yield and higher temperature generally gives >90% gas yield. However, if the reaction temperature is above 850°C, reaction kinetics do not change significantly with temperature. This is evident by the similar H₂:CO ratio obtained at 850°C and 900°C as shown in Figure 21 (1.97 and 2.02 respectively). Unexpectedly, for a few tests conducted on both FeMo-ZSM-5 and FeMo-CNF catalyst, the H₂:CO ratio was low around 1.4 to 1.8. Increase in reaction temperature causes higher coke deposition on the FeMo-ZSM-5 catalyst as compared to the FeMo-CNF catalyst. The CNF catalyst has better resistance to coke deposition. Amorphous coke deposition on the FeMo-CNF catalyst was much lower as compared to the FeMo-ZSM-5 catalyst as seen in Table 10. Crystalline coke deposition in the form of carbon nanotubes and nanofibers could be achieved on the CNF supported catalyst as already existing carbon chains allow for further growth of the nanofibers. This phenomenon was also observed in one of similar studies published on carbon nanotube formation in methane pyrolysis [119]. Carbon nanofiber structure has been observed to alter the reaction pathway of amorphous coke deposition by lowering the barrier for C-C chain growth leading to crystalline coke deposition. This phenomenon is still being investigated using DFT modelling of the CH₄ – CO₂ activated biomass gasification. The reaction is being modelled on Fe - β -Mo₂C catalyst. Higher temperature also leads to cracking of high molecular weight compounds generally obtained in the form of liquid tar thus causing coke deposition. Although the coke and ash deposition is generally only a few mg on the CNF catalyst, it could be observed on the SEM image of CNF catalyst used 3 times. Most likely coke deposition caused blocking of active sites in the CNF catalyst. Coke deposition phenomenon on the FeMo-CNF catalyst subjected to a 900°C methane-carbon dioxide-biomass reaction for 3 times is shown in Figure 22. Figure 22a shows the CNF catalyst at 10 microns. It can be observed that probable coke deposition occurs on the original metal site. The shape of the coke deposition is interesting and could be carbon nanotube deposition as was reported earlier on Fe iron active sites[120,121]. It was shown in previous studies on Fe-

Mo/ZSM-5 catalyst that coke deposition on metal active sites occur in 3-dimensional form. Carbon nanotube formation on the active sites shields active sites from deactivation. Formation of 3D structure on the possibly metal site on CNF catalyst can be clearly observed at a scale of $2\mu\text{m}$ in Figure 22b. It was observed from the previous study on methane activated biomass gasification that coke deposition increased with temperature from 850°C to 950°C while the $\text{H}_2:\text{CO}$ ratio only slightly increased from 6 to 7. High temperature is better from the thermodynamics point of view as both CO_2 reforming and steam methane reforming are endothermic reactions.

Thermodynamics is a dominant factor when reaction temperature is less than 800°C as can be seen in Figure 21 for the reaction at 750°C . The best results in terms of $\text{H}_2:\text{CO}$ ratio, gas yield, and minimizing tar formation were obtained at reaction temperatures of 850°C and above. However, the trade-off between higher gas yield and catalyst deactivation is the deciding factor for the reaction temperature. Given coke deposition over multiple tests on the CNF catalyst, 850°C is the optimum temperature for methane-carbon dioxide-biomass reaction to obtain syngas with a $\text{H}_2:\text{CO}$ ratio of 2.

Figure 21 Hardwood biomass gasification: comparison of H₂:CO ratio and syngas composition at different temperatures. Temperature: 750°C, 850°C, 900°C; pressure: 250 psig, 380 psig, 420 psig (at respective temperatures); catalyst: Fe-Mo₂C-CNF; reaction environment: 5% CH₄, 1% CO₂, 94% N₂

Figure 22 a) FeMo-CNF catalyst image obtained at 15 kV with a working distance of 12.4 mm with scale: 10 microns b) FeMo-CNF catalyst image obtained at 15 kV with a working distance of 12.4 mm with scale: 2 microns

Table 10 Gas yield, tar yield, and coke content in terms of millimoles for catalyst and reaction conditions in the CH₄ – activated and CH₄ – CO₂ activated biomass gasification

Catalyst	CH ₄ , CO ₂ Feed (vol.%)	Temperature (°C)	Gas Yield MolesX10 ⁻³	Tar Yield MolesX10 ⁻³	Coke MolesX10 ⁻³
FeMo-ZSM-5	5, 1	750	29.3	54	12.5
	5, 0	850	65.5	28	35
	5, 1	850	50.8	21	29
Fe-Mo₂C- CNF	5, 1	750	43.6	45.8	10
	5, 1	850	82.4	10	16.7
	5, 1	900	91.2	2	21

3.2.6 Proposed reaction mechanism for methane – carbon dioxide activated biomass gasification

Proposed reaction pathway for bi-reforming (steam methane reforming and dry reforming) occurring in $\text{CH}_4 - \text{CO}_2$ assisted biomass reforming is shown in Table 11. Proposed reaction pathway here also involves same elementary reaction steps that occur in CH_4 activated biomass reforming discussed in previous section. Additional elementary steps are involved in this mechanism owing to CO_2 activation, conversion to COOH^* and further to CHO^* to finally CO^* and H^* . The methane-carbon dioxide activated based biomass gasification involves both steam methane reforming and dry reforming with hydrogen (step 5 and step 9). The rate of the forward reaction for both elementary steps k_6 (k_5 is irreversible) and k_9 must be higher than k_6 and k_9 . Reverse SMR and dry reforming is thermodynamically less likely at the reaction temperature since they are endothermic in nature. The rate of reaction for further conversion of COOH^{**} to CHO^{**} can be faster than the reversible reaction since the methane – carbon dioxide activated biomass reaction produces a higher concentration of CO than the methane – biomass reaction ($k_{10} \gg k_{-10}$). Similarly, higher CO concentrations compared to H_2 in the methane-carbon dioxide-biomass reaction could be due to hydrogenation of complex aromatics and heavy hydrocarbons which generally come out as tar.

This could be due to the higher turnover frequency for COOH^{**} conversion to CHO^{**} (elementary step 10). The reason behind the drastic reduction in the hydrogen to carbon monoxide ratio from 6 to 2 at 850°C could also be due to slow steam methane reforming ($k_6\text{CH}_4\text{-CO}_2 < k_6\text{CH}_4$). The influence of adding carbon dioxide on steam methane reforming can be understood by qualitative analysis of Fe-Mo active sites on the catalyst. Carbon dioxide probably must adsorb on Fe active sites and competes with methane. Mo / Mo₂C active sites are possibly largely occupied by biomass oxygen. The gas phase methane and steam adsorbate reaction are unlikely compared to the reaction of adsorbed methane and steam adsorbate. This could explain why the thermodynamically challenging carbon dioxide activation is evidently feasible. The small amount of hydrogen in atomic form that is produced by steam methane reforming and water gas shift reactions is consumed for dry reforming thus largely driving the reaction forward. The forward reaction rates of elementary steps 3 and 7 are much higher than the reverse reaction ($k_3 \gg k_{-3}$, $k_7 \gg k_{-7}$). This means that oxygen present in the form of alcohol, phenol, carboxylic, or carbonyl functional group in biomass (only alcohol oxygen reaction steps are shown here) largely occupies the oxyphilic Mo

/ Mo₂C active sites. Adsorption of methane on the Fe active site could be somewhat hindered meaning k_1 is close to k_2 because carbon dioxide possibly occupies some Fe active sites that could have previously adsorbed methane. Thus, the hydrogen to carbon monoxide ratio in methane – carbon dioxide activated biomass gasification is always close to 2 and less than 2 in some instances. The reaction pathway shown in Table 11 is representative of reactions possibly occurring in a typical methane – carbon dioxide – biomass test.

Table 11 Proposed reaction mechanism with elementary steps in methane – carbon dioxide activated catalytic biomass gasification through bi-reforming (steam methane and CO₂ dry reforming)

$\begin{array}{c} k1 \\ \text{CH}_{4(g)} + * \rightleftharpoons \text{CH}_4^* \\ k-1 \end{array}$	Elementary Step 1 – methane adsorption on the active site
$\begin{array}{c} k2 \\ [\text{R} - \text{C} - \text{OH}]_{(g)} + * \rightleftharpoons [\text{R} - \text{C} - \text{O}^*\text{H}] \\ k-2 \end{array}$	Elementary Step 2 – selective adsorption of functional group oxygen atom of the lignocellulosic biomass on Fe or Mo
$\begin{array}{c} k3 \\ [\text{R} - \text{C} - \text{O}^*\text{H}] + \text{H}^*_{(g)} \rightleftharpoons [\text{R} - \text{C}^+ - \text{O}^*\text{H}_2] \\ k-3 \end{array}$	Elementary Step 3 – Coordination of adsorbed oxygen with adsorbed atomic hydrogen
$\begin{array}{c} k4 \\ [\text{R} - \text{C}^+ - \text{O}^*\text{H}_2] \rightleftharpoons \text{R}' + \text{H}_2\text{O}^* \\ k-4 \end{array}$	Elementary Step 4 – H ₂ O molecule breaks off from the phenolic carbon and forms steam adsorbate
$\begin{array}{c} k5 \\ \text{CH}_4^* + \text{H}_2\text{O}^* + * \rightarrow \text{CHO}^{**} + 2\text{H}_{2(g)} + \text{H}^* \end{array}$	Elementary Step 5 – First elementary step of methane reforming with steam adsorbate from step 4
$\begin{array}{c} k6 \\ \text{CHO}^{**} + * \rightleftharpoons \text{CO}^* + \text{H}^* + * \\ k-6 \end{array}$	Elementary Step 6 – Intermediate CHO* converting to CO* and H* adsorbates
$\begin{array}{c} k7 \\ [\text{R} - \text{C} - \text{O}^*\text{H}] + \text{H}^* \rightleftharpoons [\text{R} - \text{C}^+ - \text{O}^*\text{H}_2] \\ k-7 \end{array}$	Elementary Step 7 – Further phenolic oxygens coordinate with H* atom adsorbate and follows similar kinetics as Step 3 to Step 6
$\begin{array}{c} k8 \\ \text{CO}^* + \text{H}_2\text{O}^* \rightarrow \text{CO}_2^* + \text{H}_2^* \end{array}$	Elementary Step 8 – Water gas shift reaction
$\begin{array}{c} k9 \\ \text{CO}_2^{**} + \text{H}^* \rightleftharpoons \text{COOH}^{**} + * \\ k-9 \end{array}$	Elementary Step 9 – First step in CO ₂ reforming of methane
$\begin{array}{c} k10 \\ \text{COOH}^{**} + \text{H}^* + 2* \rightleftharpoons \text{CHO}^{**} + \text{OH}^* + 2* \\ k-10 \end{array}$	Elementary Step 10 – Displacement step where hydroxyl group breaks from COOH** to form CHO* using hydrogen from methane
$\begin{array}{c} k11 \\ \text{CHO}^{**} + 3* \rightleftharpoons \text{CO}^{**} + \text{H}^* + 2* \\ k-11 \end{array}$	Elementary Step 11 – hydrogen detaches from CHO**
$\begin{array}{c} k12 \\ \text{CO}^{**} \rightleftharpoons \text{CO}_{(g)} + 2* \\ k-12 \end{array}$	Elementary Step 12 – CO** release into gas phase
$\begin{array}{c} k13 \\ \text{CO}^* \rightleftharpoons \text{CO}_{(g)} + * \\ k-13 \end{array}$	Elementary Step 13 – CO* desorption
$\begin{array}{c} k14 \\ \text{CO}_2^* \rightleftharpoons \text{CO}_{2(g)} + * \\ k-14 \end{array}$	Elementary Step 14 – CO ₂ * desorption
$\begin{array}{c} k15 \\ 2\text{H}^* \rightleftharpoons \text{H}_{2(g)} + * \\ k-15 \end{array}$	Elementary Step 15 – H* atom adsorbates combine to form gas phase H ₂
$\begin{array}{c} k16 \\ \text{H}_2^* \rightleftharpoons \text{H}_{2(g)} + * \\ k-16 \end{array}$	Elementary Step 16 – H ₂ * desorption

Chapter 4 Catalyst Design and Novel Reaction Pathway of Methane Assisted Biomass Reforming

Figure 23 Schematic showing methane assisted biomass reforming on Fe / Ni / Pd – Mo₂C (metal-metal carbide) active sites on graphene nanosheet support.

4.1 Catalyst characterization

4.1.1 SEM-EDX elemental mapping

Figure 24(a, b) shows SEM-EDX generated dispersion images of Fe and Mo₂C active sites. Similarly Figure 24(c, d) show dispersion of Ni and Mo₂C dispersion at 50μm. High dispersion of Fe / Ni and β-Mo₂C nanoparticles was observed in both the catalysts. Presence of nanoclusters is also confirmed by XRD determined particle size and mean particle size from TEM size distribution (Table 12). EDX mapping of the Ni-Mo₂C active sites was also performed at higher magnification (2μm). These maps are important to show the dispersion of active sites in the catalyst support. At low magnification (100μm to 50μm), TM and Mo₂C are well-dispersed. Alloy formation between TM and β-Mo₂C was not seen in the EDX phase mapping (not shown here) as also confirmed by XRD measurements. DFT measurements and modelling of the methane assisted p-cresol reforming reaction indicates that activity of TM added to β-Mo₂C crystals was higher than that of

TM replaced β -Mo₂C crystals. Close proximity of TM and β -Mo₂C without actual phase mixing / alloy formation is possibly the reason behind synergistic activity of both TM and β -Mo₂C. Independent role of the two the active centers is discussed in later sections.

Applying basic image processing techniques on the EDX map overlay of Ni-L and Mo-L scans, average spatial separation was calculated between location of Ni and Mo₂C nanoparticles at high magnification of 2 μ m (2000 nm). 100 randomized pairs of nearest Ni, Mo₂C neighbors were selected and distance was calculated by comparing with the mapping scale. Distribution of 2D spatial separation between Ni and Mo₂C is presented in Figure 25a). Figure 25b) shows the actual EDX map obtained at high resolution. Color contrast of Ni and Mo₂C in Figure 25b) is poor due to the low loading concentration of Ni and Mo₂C. The yellow markers in Figure 25b) indicate the location of Ni-Mo₂C nanoclusters. 23% of the Ni-Mo₂C pairs were spatially separated by less than 50 nm. 56% Ni particles were separated from Mo₂C by less than 100. 42% of Ni particles were between 100 to 270 nm from Mo₂C. Mean separation between Ni and Mo₂C was calculated as 98 nm. Similar dispersion patterns are also observed in the Fe-Mo₂C-GNS catalyst.

Figure 24 Energy Dispersive X-ray (EDX) images of Fe-Mo₂C-GNS and Ni-Mo₂C-GNS catalysts a) Fe dispersion in Fe-Mo₂C-GNS, b) β -Mo₂C dispersion in Fe-Mo₂C-GNS, c) Ni dispersion in Ni-Mo₂C-GNS, d) β -Mo₂C dispersion in Ni-Mo₂C-GNS

Figure 25 a) Distribution of 2D spatial separation between Ni and β -Mo₂C nanoparticles obtained from dataset of 100 randomized nearest neighbor pairs of Ni, β -Mo₂C b) EDX overlay map of Ni-L and Mo-L obtained at magnification of 2 μ m – yellow markers are added to indicate the location of Ni-Mo₂C nanoclusters.

4.1.2 Powder x-ray diffractometry:

Figure 26 shows XRD peaks in the catalysts and Table 12 shows crystal size calculated from Scherrer equation applied using Full Width Half Maximum (FWHM) values of XRD peaks. XRD measurements revealed the existence of metal-metal carbide active sites. β - Mo_2C peaks were observed in Fe- Mo_2C -GNS fresh and spent catalysts (after CH_4 – p-cresol reaction) at $2\theta = 34.8^\circ$, 38.3° , 39.8° , 52.6° , 62.2° , 70.1° , 75.5° , and 76.5° . [122–124] β - Mo_2C peaks in Ni- Mo_2C -GNS were observed at 34.8° , 38.04° , 39.56° , 61.7° , 74.7° , and 75.7° . [125] In the case of Pd- Mo_2C -GNS, a sharp β - Mo_2C peak was observed at 68.52° , and a broad peak was observed between 36.7° to 37.9° . The shift in β - Mo_2C peaks from Fe- Mo_2C -GNS to Pd- Mo_2C -GNS could be attributed to change in lattice parameters and difference in ionic radii of doped and dopant ion. In the case of Fe- Mo_2C -GNS, no characteristic Fe or Fe_3C peaks were recorded around 44.5° and 45° indicating uniform dispersion of Fe added on Mo_2C . In the case of Ni- Mo_2C -GNS fresh and spent catalysts, Ni in metallic state was observed at 44.2° as a shoulder in the broader peak at 43.5° indicating the presence of crystalline graphitic carbon reflection at (100) [122,125,126]. Pd (111) and Pd(200) peaks were observed at 40.42° and 46.9° in the case of Pd- Mo_2C -GNS fresh and spent catalysts. [123,127] In all the three catalysts, alloy formation of TM and β - Mo_2C was not observed clearly indicating presence of dual active sites. Characteristic peak indicating the presence of graphitic carbon at 43.5 and a broad peak at 26.5° was observed in the case in Ni- Mo_2C -GNS and Pd- Mo_2C -GNS catalysts but was very weak in the case of Fe- Mo_2C -GNS. [122]

Figure 26 PXRD patterns of Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS fresh and spent catalysts for methane assisted p-cresol reforming reaction

Table 12 Mean particle size from TEM images particle size distribution (PSD), XRD peak analysis (Scherrer equation), I_D/I_G values from Raman spectroscopy measurements

Catalyst	Elements	Mean particle size (nm)		I_D/I_G
	Identified from TEM, XRD, SEM, XPS	XRD peak analysis (FWHM based values)	TEM particle size distribution	Obtained from Raman spectroscopy
fresh Fe-Mo₂C-GNS	Fe / Fe ₃ C	16.5	13.5	0.88
	β -Mo ₂ C	23.4		
spent Fe-Mo₂C-GNS	Fe / Fe ₃ C	10	11.7	0.98
	β -Mo ₂ C	24.3		
fresh Ni-Mo₂C-GNS	Ni	10.5	8.7	0.70
	β -Mo ₂ C	24.3		
spent Ni-Mo₂C-GNS	Ni	13.7	9.3	0.76
	β -Mo ₂ C	25		
fresh Pd-Mo₂C-GNS	Pd	26	20.4	0.77
	β -Mo ₂ C	23.3		
spent Pd-Mo₂C-GNS	Pd	27	13	0.84
	β -Mo ₂ C	21.6		

4.1.3 Transmission electron microscopy (TEM) imaging and particle size distribution

Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalysts were imaged in the TEM to study particle size. Figure 27, Figure 28, and Figure 29 show TEM images, particle size distribution of fresh and spent catalysts. EDX elemental microanalysis is shown in Figure 27(e), Figure 28(e), and Figure 29(e) for the fresh catalysts. From Table 12, TEM mean particle size decreased after the reaction. XRD calculated crystal size of Fe / Fe₃C particles decreased by ~40% after the reaction (16.5→10 nm). Similar trend was observed with Pd-Mo₂C-GNS catalyst where TEM mean particle size decreased substantially by ~37%. However, TEM mean particle size and XRD calculated Ni particle size slightly increased after the reaction indicating agglomeration to some extent. Particle size distribution became highly skewed with most of the particle of size less than 20 nm in the spent Fe-Mo₂C-GNS catalyst.

Figure 27 TEM images of Fe-Mo₂C-GNS a) fresh synthesized catalyst at resolution of 50 nm, b) spent catalyst after reaction at resolution of 100 nm; particle size distribution: c) fresh catalyst with mean size of 13.5 nm, d) spent catalyst with mean size 11.7 nm, e) EDS microanalysis performed with JEOL TEM at 100 nm, ‘*’ indicates Mo peaks and ‘♦’ indicates Fe peaks

Figure 28 TEM images of Ni-Mo₂C-GNS a) fresh synthesized catalyst at resolution of 100 nm, b) spent catalyst after reaction at resolution of 100 nm; particle size distribution: c) fresh catalyst with mean size of 8.7 nm, d) spent catalyst with mean size 9.3 nm; e) EDS microanalysis performed with JEOL TEM at 100 nm, ‘*’ indicates Mo peaks and ‘♥’ indicates Ni peaks

Figure 29 TEM images of Pd-Mo₂C-GNS a) fresh synthesized catalyst at resolution of 100 nm, b) spent catalyst after reaction at resolution of 200 nm; particle size distribution: c) fresh catalyst with mean size of 20.4 nm, d) spent catalyst with mean size 12.9 nm; e) EDS microanalysis performed with JEOL TEM at 100 nm, ‘*’ indicates Mo peaks and ‘♣’ indicates Pd peaks

In the case of Ni-Mo₂C-GNS, Figure 28 (c, d), particle size distribution skewed with 70% particles between 5 to 10 nm in the fresh catalyst. Near normal distribution was observed in the spent Ni-Mo₂C-GNS. Size distribution was nearly symmetric on the Pd-Mo₂C-GNS catalyst before and after reaction but the mean particle size decreased drastically from 20.4 nm in fresh Pd-Mo₂C-GNS to 12.5 nm in the spent catalyst (Figure 29(c, d), Table 12). TEM imaging of the catalysts provides key insights for particle size distribution, dispersion of TM, β -Mo₂C in the GNS support, and elemental composition. Additional TEM images are provided in Figure 30.

a) fresh Fe-Mo₂C-GNS

b) spent Fe-Mo₂C-GNS

c) fresh Ni-Mo₂C-GNS

d) spent Ni-Mo₂C-GNS

e) fresh Pd-Mo₂C-GNS

f) spent Pd-Mo₂C-GNS

Figure 30 Additional TEM images of fresh and spent Fe-Mo₂C-GNS(a, b), fresh and spent Ni-Mo₂C(c, d), fresh and spent Pd-Mo₂C(e, f)

4.1.4 X-Ray photoelectron spectroscopy (XPS)

XPS detail spectral scans for Mo 3d and C 1s for Fe-Mo₂C-GNS and Ni-Mo₂C-GNS were obtained and peak analysis was performed using Gaussian fit in Origin Student 2020 version (Figure 31). Mo 3d peak at 228.6 eV was observed in the detail spectra of both catalysts and is associated to the Mo²⁺ peak of β -Mo₂C. Other peaks observed at binding energies: 229.8, 231.9, 232.5, and 233 in the Fe-Mo₂C-GNS and Ni-Mo₂C-GNS were attributed to Mo ^{δ +} where $4 < \delta < 6$. [128,129] These peaks were observed stronger compared Mo₂C possibly due to surface oxidation and molybdenum oxycarbide formation in the freshly prepared catalyst. XPS analysis was performed within 2 hours of catalyst preparation using pyrolysis and loaded in the XPS chamber with as low air exposure as practically possible without a vacuum chamber or glove box. Thus, some oxidation may have still occurred on the Mo₂C surface. Similarly, Mo 3d peak at 235.7 eV is attributed to MoO₃. [130] Nonetheless, the characteristic Mo₂C peak is observed at 228.6 eV. According to Chen et al, alloy formation with Fe and Ni lowers the binding energy of the Mo₂C peak. For 2% Fe-Mo₂C and 2% Ni-Mo₂C, Chen et al reported Mo₂C BE of 228.4 eV and 228.58 eV respectively [131]. Considering the existing evidence from XRD measurements, it can be concluded that alloy formation was not observed between TM and β -Mo₂C. Due to low loading concentration of Fe and Ni (0.5 wt.% each), detailed 2p XPS spectra did not yield useful information as concentration is below the resolution of the instrument. C 1s spectra was obtained for both the catalysts and a clear peak for sp² hybridized graphitic carbon was observed at 284.6 eV.

Figure 31 XPS detail scans a) Mo 3d b) C1s for Fe-Mo₂C-GNS c) Mo 3d, d) C 1s for Ni-Mo₂C-GNS.

4.1.5 Thermogravimetry analysis for weight loss studies in GNS supported catalysts

TGA oxidation was performed to observe the effect of high temperature oxidizing environment on the graphene nanosheets (GNS) support in fresh and spent catalysts. Although the reactions were typically performed in non-oxidative environment, syngas products viz. H₂O, CO, CO₂ may generate oxidizing effect on the catalyst support. Figure 32 shows weight loss relative to temperature in TGA oxidation tests for fresh and spent catalysts. Barring the outliers viz. fresh Ni-Mo₂C-GNS and fresh Pd-Mo₂C-GNS, weight loss in the transition metal doped Mo₂C-GNS

catalysts was between 15% to 27%. All three catalysts subjected to high temperature reaction sustained the core graphene nanosheets (GNS) support structure. Weight loss in fresh and spent catalysts was mainly due to oxidation of amorphous coke at temperatures less than 500°C crystalline coke on active sites at temperatures >500°C. 11.25 and 9.2 wt.% crystalline coke was observed on Fe-Mo₂C-GNS and Ni-Mo₂C-GNS respectively.

4.1.6 Raman spectroscopy

Figure 33 shows Raman spectra of fresh and spent Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalysts. Spent catalysts were subjected to CH₄ assisted biomass reforming reaction at 1073 K. Biomass reforming would cause higher coke and ash deposition along with other impurities having highest impact on crystallinity of GNS support compared to p-cresol and lignin. Two peaks were observed at 1350 cm⁻¹ and 1580 cm⁻¹ indicate disordered and ordered graphitic carbon respectively. Disordered carbon peak around 1350 cm⁻¹ is referred to as D peak (disordered carbon) and graphitic carbon peak at 1580 cm⁻¹ is G-peak (graphitic carbon). Ratio of peak intensities I_D/I_G is an indication of the quality of graphene nanosheets / nanotubes present in the catalyst support. Lower I_D/I_G ratio indicates higher quality of graphitic carbon / nanofibers with lesser defects. From Figure 11, fresh Ni-Mo₂C-GNS showed the lowest I_D/I_G ratio of 0.7 and spent Fe-Mo₂C-GNS catalyst had highest I_D/I_G ratio of 0.98. Amorphous or disordered carbon was higher in spent Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS (I_D/I_G 0.76, 0.98, and 0.84 respectively). This could be due to amorphous coke deposition on the spent catalyst subjected to high-temperature methane assisted biomass reforming. Defects in the pristine graphene nanosheets increases post-reaction due to deposition of amorphous and crystalline coke and harsh reaction conditions.

Figure 32 TGA oxidation tests of fresh and spent Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, Pd-Mo₂C-GNS with 1% O₂ from temperature 22°C (295 K) to 850°C (1123 K) (flow rate: 1 sccm O₂, 99 sccm He)

Figure 33 Raman spectra of fresh and spent Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalysts. Spent catalysts were subjected to methane assisted p-cresol reforming at 800°C (1073K).

4.2 Methane assisted p-cresol reforming

Experimental investigation for the role of TM and β -Mo₂C on GNS support was performed using p-cresol as a model compound for representing lignin / biomass oxygenates. Based on the proposed reaction pathway in the previous study, p-cresol was chosen to obtain experimental and first-principles based (DFT) understanding of selective cleavage of C-OH over C-CH₃ bond. Selective HDO reforming of biomass oxygenates through CH₄ activation leads to higher syngas yield and hydrogen rich syngas generation. Three transition metals were chosen along with β -Mo₂C for detailed insights on catalyst performance. Fe and Ni were also synthesized without β -Mo₂C to evaluate the standalone performance of these transition metals. β -Mo₂C was also used as a catalyst on the GNS support without adding a transition metal to understand the catalytic effect of

molybdenum carbides. Bi-metallic TM and β -Mo₂C catalysts were synthesized with 0.5 wt.% TM (Fe, Ni, Pd) with 4 wt.% β -Mo₂C. Performance of Fe-Mo₂C and Ni-Mo₂C catalyst was compared with Pd-Mo₂C. Pd nanoparticles on activated carbon / CNT support have shown excellent activity for conversion of biomass oxygenates and for activation of methane.[119,120,132]

Figure 34(a, b) shows syngas composition obtained from p-cresol, H₂:CO ratio, HDO conversion, and hydrogen-based conversion. Reforming performed over Ni-Mo₂C-GNS and Pd-Mo₂C-GNS resulted in high H₂:CO ratio (3.88, 3.5) and higher HDO conversion (~82%). Fe-Mo₂C-GNS catalyzed p-cresol reforming resulted in lower H₂:CO ratio and HDO, hydrogen-based conversion compared to the Ni and Pd added catalysts. Mo₂C-GNS catalyst performance was poor compared to the TM added Mo₂C catalyst in terms of H₂:CO ratio, lowest HDO and H₂ conversion (73% and 35% respectively). Catalyst performance in terms of overall carbon balance of CH₄ assisted p-cresol reforming reaction is shown in Table 4. Gas yield was only 28 mol.% on the Mo₂C-GNS catalyst with high coke deposition and liquid tar formation of ~26 mol.%. Performance of Mo₂C-GNS was below average compared to TM added Mo₂C-GNS catalysts. With addition of 0.5 wt.% of TM (Fe / Ni / Pd), gas yield improved to an average of 35% with relatively low coke deposition and liquid tar formation. Overall carbon balance for reactions performed on Fe-Mo₂C-GNS was better compared to those on Ni-Mo₂C and Pd-Mo₂C. Higher gas yield of 40 mol.%, lower tar and coke formation (22, 19 mol.% respectively) was observed in reactions performed on the Fe-Mo₂C-GNS catalyst. Higher H₂:CO ratio was 3.2 and 2.8 over Fe-GNS and Ni-GNS catalysts was the result of direct catalytic methane dehydrogenation at higher temperatures. Direct methane dehydrogenation is thermodynamically favored on Fe and Ni catalysts at higher temperatures. This phenomenon is also evident from significantly higher coke deposition over Fe-GNS (35 mol.%) and Ni (48 mol.%) as seen in Table 13. Coke deposition was relatively low on the Mo₂C-GNS catalyst (27 mol.%).

Based on the observed performance of the TM added Mo₂C-GNS against Mo₂C and TM catalysts, it was hypothesized that CH₄-assisted p-cresol reforming reaction requires two bi-functional active sites (dual active sites). Addition of transition metals (Fe / Ni / Pd) causes higher HDO reforming of p-cresol, results in higher turn-over-frequency (TOF) apparent from the gas yield, and lowers tar, coke formation.

Following major reactions constitute the reaction pathway for p-cresol reforming:

Initial reactions require bi-functional active sites (dual centers):

Possibly on TM (Fe/Ni/Pd) site: $\text{CH}_4^* \rightarrow \text{C}^* + 4\text{H}^*$ equation (12)

Possibly on Mo_2C site: $\text{CH}_3\text{-C}_6\text{H}_4^*\text{-O}^*\text{H}$ (p-cresol) + $\text{H}^* \rightarrow \text{CH}_3\text{-C}_6\text{H}_4^* + \text{H}_2\text{O}^*$.equation (13)

Overall initial reaction:

p-cresol + CH_4 --> Toluene + CO + 2H_2 $\Delta\text{H} = 183.3 \text{ kJ mol}^{-1}$ (1.9 eV).....equation (14)

Elementary reaction steps in the CH_4 assisted p-cresol reforming pathway are discussed in detail in the later section from first principles (DFT) based calculations. The degree of p-cresol HDO reforming is directly proportional to the syngas yield and inversely proportional to coke formation. If higher degree of HDO reforming occurs, C^* from CH_4 will be converted to CO, CO_2 products. However, without a strong oxophilic active site like Mo_2C , p-cresol adsorption will be hindered by incoming methane which is adsorbed easily on the transition metal sites. Mo_2C strongly binds p-cresol as seen in the DFT results in the following section. Experimental insights on requirement of dual active sites (2 bi-functional active sites) was the motivation for the integrated DFT based thermodynamic and micro-kinetic investigation discussed in the following section

Table 13 Overall carbon balance-gas yield, tar yield, coke yield, and unaccounted carbon from CH₄ assisted p-cresol reforming over Fe, Ni, Pd & Mo₂C catalysts

Catalyst (GNS support)	Gas yield (mol.%)	Tar condensate (mol.%)	Coke (mol.%)	Unaccounted C (mol.%)
Fe	29.3	28.2	34.7	7.8
Ni	26.2	16.4	47.6	9.8
Mo₂C	27.8	25.8	27	19.4
Fe-Mo₂C	40.1	22.3	19.3	18.3
Ni-Mo₂C	29.3	18.8	24.4	27.5
Pd-Mo₂C	38.6	17.6	25.6	18.2

a)

b)

Figure 34 a) Syngas product composition of methane assisted p-cresol reforming reaction over six catalysts at temp: 1073K b) H₂:CO, HDO conversion, and H₂ based conversion for CH₄ assisted p-cresol reforming performed over six catalysts.

4.3 Results and discussion on Density Functional Theory (DFT) calculations for catalytic methane assisted p-cresol reforming over Fe / Ni / Mo₂C active sites

Adsorption energies of the reactant, products and intermediates formed in the methane assisted reforming of p-cresol over the pure Mo₂C and Ni and Fe doped Mo₂C surfaces calculated using DFT method were listed in Table 14.

Table 14 Comparison of adsorption energy at pure Mo₂C(001) vs Fe and Ni doped Mo₂C(001) surfaces. *Gas-phase energy of C₇H₇-OH was used as reference for adsorbed C₇H₇-OH and dissociated C₇H₇+OH; gas-phase energy of CO used for adsorbed CO and dissociated C+O; whereas gas-phase energy of CH₄ and H₂ is used for dissociated C+4H and H+H, respectively.

Surface	Adsorption Energies* (eV)						
	C ₇ H ₇ -OH	C ₇ H ₇ +OH	C ₇ H ₈	C+4H	C+O	CO	H+H
Mo ₂ C	-1.97	-2.62	-1.83	-2.57	-3.67	-2.17	-1.70
Fe-r-Mo ₂ C	-1.63	-2.66	-1.79	-1.66	-2.89	-2.12	-1.36
Ni-r-Mo ₂ C	-1.64	-2.69	-1.83	-1.99	-2.47	-2.42	-1.51
Fe-a-Mo ₂ C	-1.43	-2.33	-1.66	-1.34	-2.87	-2.15	-1.15
Ni-a-Mo ₂ C	-1.39	-2.24	-1.74	-1.32	-2.80	-2.07	-1.13
Ni-strip-a-Mo ₂ C	-0.73	-1.41	-0.93	0.58	-1.66	-1.26	-0.40
Ni(111)	-1.25	-1.77	-1.15	0.90	0.07	-1.11	-0.78

Lignin model molecule p-cresol (H₃C-C₆H₄-OH) bind to the Mo₂C surface using its π electron in a flat 3 σ configuration, as shown in Figure 35(a). In the 3 σ configuration the p-cresol from three sigma bonds with three different Mo atoms (Figure 35(a)). The adsorption energy of p-cresol was calculated to be -1.97 eV (Table 14). Binding of p-cresol was found to be similar over the Fe-r-Mo₂C and Ni-r-Mo₂C surfaces, as shown in Figure 35(b) and Figure 35(c), respectively. Over the Fe-a-Mo₂C and Ni-a-Mo₂C surfaces p-cresol bind in a flat 2 σ binding mode making two sigma bond with two surface Mo atoms, whereas the O atom of the OH group interact with the Fe and Ni ad-atom, as shown in Figure 35(d) and Figure 35(e), respectively. The binding energy trend of p-cresol over the catalytic surfaces studied here has been shown in Figure 38, where the binding

energy decreases in the order Mo_2C (-1.97 eV) > $\text{Ni-r-Mo}_2\text{C}$ (-1.64 eV) ~ $\text{Fe-r-Mo}_2\text{C}$ (-1.63 eV) > $\text{Fe-a-Mo}_2\text{C}$ (-1.43 eV) ~ $\text{Ni-a-Mo}_2\text{C}$ (-1.39 eV). During the HDO process, the adsorbed p-cresol undergo C-O bond cleavage to form adsorbed $\text{H}_3\text{C-C}_6\text{H}_5$ and OH intermediates, as shown in Figure 39. The reaction energy of the C-O bond dissociation was calculated to be exothermic over the pure and TM doped Mo_2C surfaces (Figure 38(b)). The exothermic nature of the C-O bond cleavage reaction over the pure and TM-doped Mo_2C surface will facilitate the reforming of p-cresol reaction. The dissociation of methane was favorable over all the five catalytic surfaces studied (Table 14), with the reaction energy following the trend: Mo_2C (-2.57 eV) > $\text{Ni-r-Mo}_2\text{C}$ (-1.99 eV) > $\text{Fe-r-Mo}_2\text{C}$ (-1.66 eV) > $\text{Fe-a-Mo}_2\text{C}$ (-1.34 eV) ~ $\text{Ni-r-Mo}_2\text{C}$ (-1.32 eV), as has been shown in Figure 38(c). During the methane assisted p-cresol reforming desorption of C and O adsorbed species as CO(g) and adsorbed H atoms as $\text{H}_2\text{(g)}$ are two very important step. Adsorption geometry of the co-adsorbed C+O has been shown in Figure 36. During the reforming reaction the co-adsorbed C and O will initially form adsorbed CO at the catalyst surface which will eventually desorb as CO(g) . Geometry of the CO adsorption to the five catalyst surfaces studied here has been shown in Figure 36, whereas the adsorption energies are tabulated in Table 14. The reaction energy of co-adsorbed C+O to CO(g) was calculated to be highly endothermic for all the five catalyst surfaces, as shown in Figure 38(e). As can be seen from Figure 38(e), the formation of CO(g) from adsorbed C+O was most difficult over the pure Mo_2C surface (3.67 eV) and the addition of Fe and Ni significantly reduced the desorption energy barrier. The $\text{Ni-r-Mo}_2\text{C}$ surface was calculated to have the lowest desorption barrier 2.47 eV, which is 1.2 eV lower than the pure Mo_2C . The C+O desorption barrier for $\text{Fe-r-Mo}_2\text{C}$, $\text{Fe-a-Mo}_2\text{C}$ and $\text{Ni-a-Mo}_2\text{C}$ were calculated to be 2.89 eV, 2.87 eV and 2.80 eV, respectively, all significantly lower compared to the pure Mo_2C . Similar behavior also observed for the desorption of chemisorbed H+H to $\text{H}_2\text{(g)}$ (Figure 38(d)), following the trend: $\text{Ni-a-Mo}_2\text{C}$ (1.13 eV) < $\text{Fe-a-Mo}_2\text{C}$ (1.15 eV) < $\text{Fe-r-Mo}_2\text{C}$ (1.36 eV) < $\text{Ni-r-Mo}_2\text{C}$ (1.51 eV) < Mo_2C (1.70 eV). DFT optimized geometries of chemisorbed hydrogen over the pure and TM doped Mo_2C surfaces are shown in Figure 37.

Figure 35 DFT optimized geometry of p-cresol over (a) Mo₂C, (b) Fe-r-Mo₂C, (c) Ni-r-Mo₂C, (d) Fe-a-Mo₂C and (e) Ni-a-Mo₂C catalyst surfaces. Color code: Mo (turquoise), Fe (violet), Ni (green), O (red), C (black), H (white).

Figure 36 DFT optimized geometry of H₃C-C₆H₄+OH dissociated state after the C-O bond cleavage of p-cresol over (a) Mo₂C, (b) Fe-r-Mo₂C, (c) Ni-r-Mo₂C, (d) Fe-a-Mo₂C and (e) Ni-a-Mo₂C catalyst surfaces. Color code: Mo (turquoise), Fe (violet), Ni (green), O (red), C (black), H (white).

Figure 37 DFT optimized geometry of chemisorbed H_2 over (a) Mo_2C , (b) $Fe-r-Mo_2C$, (c) $Ni-r-Mo_2C$, (d) $Fe-a-Mo_2C$ and (e) $Ni-a-Mo_2C$ catalyst surfaces. Mo (turquoise), Fe (violet), Ni (green), H (white).

A free energy diagram of the complete cycle of methane reforming of p-cresol at temperature 1073 K has been shown in Figure 39. The adsorption free energy of $H_3C-C_6H_4-OH$ (Figure 39(a→b)) was calculated to be uphill by 1.87 eV over Mo_2C surface, which increases to ~2.2 eV over $Ni-r-Mo_2C$ and $Fe-r-Mo_2C$ surfaces and ~2.4 eV over the $Ni-a-Mo_2C$ and $Fe-a-Mo_2C$ surfaces, clearly indicating the preferable adsorption of the p-cresol over the Mo_2C surface. As discussed before the C-O bond dissociation of adsorbed $H_3C-C_6H_4-OH$ is favorable over the pure and TM-doped Mo_2C surface, as shown in (Figure 39(b→c)). The dissociative chemisorption of CH_4 to chemisorbed CH_3 and H (Figure 39(c→d)) were calculated to be endergonic over all the five surfaces. The successive C-H dissociation of CH_3+H to $C+4H$ (Figure 39(d→e)) were exergonic for Mo_2C , $Fe-r-Mo_2C$ and $Ni-r-Mo_2C$ surfaces, whereas almost energetically neutral over the $Fe-a-Mo_2C$ and $Ni-a-Mo_2C$ surfaces. The dissociated $H_3C-C_6H_4$ intermediate hydrogenated in the next step (Figure 39(e→f)) to produce toluene ($C_6H_5-CH_3$) which was subsequently desorbed from the surface as shown in (Figure 39(f→g)). Both the hydrogenation and desorption steps found to be highly favorable over both the Mo_2C and TM doped Mo_2C surfaces, as can be seen from Figure 39. This suggest that both the pure Mo_2C and TM doped Mo_2C surfaces will be highly active for the dissociation of the p-cresol and CH_4 molecule. However, over the pure Mo_2C surface, the formation of CO from co-adsorbed C and O was found to be uphill in energy by 1.5 eV (Figure 39(g→h)). The presence of Fe and Ni reduced the energy of this endergonic step to ~0.7 eV over the $Fe-r-Mo_2C$, $Fe-a-Mo_2C$ and $Ni-a-Mo_2C$ surfaces, and almost zero over the $Ni-r-Mo_2C$ surface (Figure 39(g→h)). The desorption of adsorbed CO (Figure 39(h→i)) was found to be favorable over the Mo_2C , $Fe-r-Mo_2C$, $Fe-a-Mo_2C$ and $Ni-a-Mo_2C$ surface, whereas over the $Ni-r-Mo_2C$ surface the step was energetically uphill by a small barrier 0.22 eV. The catalytic cycle was

completed with the adsorbed H's were desorbed as $H_2(g)$ as shown in (Figure 39(i→j)). The desorption of chemisorbed H atoms as $H_2(g)$ was found to be endergonic by 0.49 eV and 0.12 over the Mo_2C and Ni-r- Mo_2C surfaces, whereas the step is energetically favorable over the Fe-r- Mo_2C , Fe-a- Mo_2C and Ni-a- Mo_2C surface by -0.19 eV, -0.61 eV and -0.65 eV, respectively. The overall methane reforming of p-cresol to toluene, CO and H_2 was found to be energetically favorable with free energy (G-TS) calculated to be -1.1 eV at the experimental temperature 1073 K. The free energy diagram shown in Figure 39 indicates over the pure Mo_2C surface the desorption of the adsorbed C, O and H may be difficult due to high uphill energy from lowest energy intermediate Figure 39(g) to the final product Figure 39(j). The promotional role of Ni and Fe is lowering the endergonic desorption step and hence helping in the formation of CO and H_2 gas-phase species, as seen in the experiment with Ni-Mo and Fe-Mo catalysts having higher syngas yield compared to pure Mo catalyst.

Figure 38 Comparison of reaction enthalpy (ΔH) of (a) p-cresol adsorption, (b) dissociation of adsorbed p-cresol, (c) CH_4 dissociation, gas-phase formation (d) H_2 desorption and (e) CO desorption at the pure and transition metal doped $Mo_2C(001)$ surfaces.

Figure 39 Free Energy (E-TS) diagram of the methane assisted p-cresol reforming reaction over pure and transition metal doped $\text{Mo}_2\text{C}(001)$ surfaces supported over GNS (Temperature = 1073 K)

4.3.1 CH_4 assisted p-cresol reforming reaction on larger cluster and metallic surface

Ni strip (atomic layer) was adsorbed and relaxed on the Mo_2C cluster to observe the effect of adding a larger metal cluster on the Mo_2C surface. CH_4 assisted p-cresol reforming reaction was also studied on the Ni(111) surface cleaved from Ni-FCC(111). Adsorption energies of the reactant, products and intermediates formed in the methane assisted reforming of p-cresol over the Ni-strip-add- Mo_2C surface calculated using DFT method were listed in Table 5. p-cresol ($\text{H}_3\text{C-C}_6\text{H}_4\text{-OH}$) bind to the Ni-strip-add- Mo_2C surface using its π electron in a flat 3σ configuration at the Mo_2C strip part, as shown in Figure 40(a). In the 3σ configuration the p-cresol from three sigma bonds with three different Mo atoms (Figure 40(a)). The adsorption energy of p-cresol was calculated to be -0.73 eV (Table S1). The adsorption of p-cresol is lower at the Ni-strip (shown in

Figure 41(a)) by 0.5 eV. The p-cresol adsorption energy at the Ni-strip-add-Mo₂C surface is lower compared to the Ni-a-Mo₂C (-1.39 eV) surface. Adsorbed p-cresol undergo C-O bond cleavage to form adsorbed H₃C-C₆H₄ and OH intermediates, as shown in Figure 6(b). Toluene (H₃C-C₆H₅) was formed after hydrogenation of the H₃C-C₆H₄ intermediate with the reaction energy calculated to be 0.04 eV. The desorption energy of toluene is calculated to be 0.93 eV (Table 14). The dissociative chemisorption of methane over Ni-strip-add-Mo₂C surface was calculated to be endothermic by 0.58 eV (Table 14). The reaction energy of co-adsorbed C+O to CO was calculated to be slightly endothermic by 0.4 eV (Table 14). The adsorbed geometry of CO molecule and dissociated co-adsorbed C+O, were shown in Figure 42(c, d) respectively. The desorption energy of adsorbed CO over the Ni-strip-add-Mo₂C surface was calculated to be 1.26 eV (Table 14). Similarly, the desorption of chemisorbed H+H (Figure 42(b)) to H₂(g) was also calculated to be endothermic by 0.4 eV (Table 14).

The DFT method is used to obtain the adsorption energies of p-cresol, dissociated H₃C-C₆H₄+OH and toluene (H₃C-C₆H₅) over the Ni(111) surface, given in Table 14. The DFT optimized geometries of the adsorbates over the Ni(111) surface are given in Figure 43. p-cresol (H₃C-C₆H₄-OH) bind to the Ni(111) surface using its π electron in a flat 3 σ configuration, as shown in Figure S11(a) with adsorption energy -1.25 eV (Table 14). Adsorbed p-cresol undergo C-O bond cleavage to form adsorbed H₃C-C₆H₄ and OH intermediates, as shown in Figure 43(b). The reaction energy is calculated to be exothermic by -0.52 eV (Table 14). The desorption energy of toluene is calculated to be 1.15 eV (Table 14). The dissociative chemisorption of methane to C+4H over Ni(111) surface was calculated to be endothermic by 0.90 eV (Table 14). The reaction energy of co-adsorbed C+O to CO was calculated to be favorable by -1.18 eV (Table 14). The desorption energy of adsorbed CO over the Ni(111) surface was calculated to be 1.11 eV (Table 14). Similarly, the desorption of chemisorbed H+H to H₂(g) was also calculated to be endothermic by 0.78 eV (Table 14).

Figure 40 DFT optimized geometry of (a) chemisorbed p-cresol ($\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{OH}$), (b) dissociative chemisorbed $\text{H}_3\text{C}-\text{C}_6\text{H}_4+\text{OH}$ and (c) chemisorbed toluene ($\text{H}_3\text{C}-\text{C}_6\text{H}_5$) over the Ni-strip-add- Mo_2C catalyst surfaces. Mo (turquoise), Ni (blue), H (white), O (red), C (black).

Figure 41 DFT optimized geometry of (a) chemisorbed p-cresol ($\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{OH}$), (b) dissociative chemisorbed $\text{H}_3\text{C}-\text{C}_6\text{H}_4+\text{OH}$ and (c) chemisorbed toluene ($\text{H}_3\text{C}-\text{C}_6\text{H}_5$) over the Ni-strip in the Ni-strip-add- Mo_2C catalyst surfaces. Mo (turquoise), Ni (blue), H (white), O (red)

Figure 42 DFT optimized geometry of dissociative chemisorbed (a) CH_3+H and (b) $\text{H}+\text{H}$, (c) chemisorbed CO and (d) dissociative chemisorbed $\text{C}+\text{O}$ over the Ni-strip-add- Mo_2C catalyst surfaces. Mo (turquoise), Ni (blue), H (white), O (red), C (black).

Figure 43 DFT optimized geometry of (a) chemisorbed p-cresol ($\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{OH}$), (b) dissociative chemisorbed $\text{H}_3\text{C}-\text{C}_6\text{H}_4+\text{OH}$ and (c) chemisorbed toluene ($\text{H}_3\text{C}-\text{C}_6\text{H}_5$) over the Ni(111) catalyst surfaces. Ni (blue), H (white), O (red), C (black).

4.3.2 Microkinetic modelling (MKM) of methane assisted p-cresol reforming

Ab-initio microkinetic modeling (MKM) developed by Medford et al. at SUNCAT, Stanford University was extensively used to obtain the catalytic rates for the production of H₂ and CO species for 7 cases discussed earlier. Figure 44 shows turn-over-frequency (TOF) over temperature for methane assisted p-cresol reforming on Mo₂C, Fe-a / r-Mo₂C, Ni-a / r-Mo₂C, Ni-strip-a-Mo₂C, and Ni(111) supported over GNS. Detailed methodology of ab initio MKM model is described in the supplementary information along with the reactions used for MKM calculations. MKM was performed over temperature range of 1073 K to 1273 K with total pressure of 1 bar and equimolar p-cresol to CH₄ ratio (1:1). As predicted by the reaction mechanism described above, hydrogen rich syngas (H₂:CO > 2) is produced at 1073 K and above. Fe-a-Mo₂C and Ni-a-Mo₂C active centers had 4 to 5 orders of magnitude higher TOF over Mo₂C, Fe-r-Mo₂C, and Ni-r-Mo₂C.

Following the reaction pathway investigated using p-cresol and CH₄ over the five surfaces, reaction energies were calculated for p-cresol adsorption over the surfaces using π electron cloud in flat 3 σ configuration (highly exothermic), CO bond dissociation from p-cresol (mildly exothermic), methane dissociation (highly exothermic), CO(g) evolution from co-adsorbed C+O (highly endothermic), and desorption of chemisorbed H+H to H₂(g) (mildly endothermic). CO desorption barrier was the highest on Mo₂C surface and lowest on Fe-a-Mo₂C and Ni-a-Mo₂C surfaces. Similar trend was also observed for H₂ desorption over the 5 surfaces. Thus MKM calculations were initially performed for CO(g) formation from co-adsorbed C* and O* and also for H*+H* $\rightarrow$ H₂(g) on the Mo₂C, Fe-r-Mo₂C, Ni-r-Mo₂C, Fe-a-Mo₂C, and Ni-a-Mo₂C surfaces and were later extended to the Ni-strip-a-Mo₂C and Ni(111) surfaces

Although, H₂ and CO production rates are of the same order of magnitude, H₂ production rate is 2 to 4 times higher as compared to CO for the Fe-a-Mo₂C and Ni-a-Mo₂C catalysts. Production rate of H₂, CO increased from $\sim 10^{-6}$ s⁻¹ to $\sim 10^{-2}$ s⁻¹ for Fe, Ni added onto the Mo₂C crystal. At 1073 K, production rates of H₂, CO was $\sim 10^{-10}$ s⁻¹ and 10^{-9} s⁻¹ for Fe-r-Mo₂C and Ni-r-Mo₂C respectively which increased to $\sim 10^{-5}$ s⁻¹ at 1273 K. H₂, CO TOF was $\sim 10^{-7}$ s⁻¹ for Mo₂C between 1073 to 1273 K which was much lower than Fe-a-Mo₂C and Ni-a-Mo₂C. Production rate of H₂ and CO over Ni-strip-a-Mo₂C were calculated to be 3.8×10^{-9} s⁻¹ and 1.9×10^{-9} s⁻¹ at 1073 K. The production rates of H₂ and CO increases to 1.2×10^{-5} s⁻¹ and 6.1×10^{-6} s⁻¹ at 1273 K. Production rates on the single active site Ni(111) surface for CH₄ assisted p-cresol reforming was very low ($\sim 10^{-17}$ s⁻¹) compared to other surfaces. Thus, the MKM model validates the theory of dual active centers contributing to

production of hydrogen rich syngas in methane assisted p-cresol reforming. MKM modelling performed over 6 surfaces here on a molecular level shows the general direction of reforming achieved in CH₄ assisted biomass reforming. The trend observed from molecular modelling and reaction enthalpy, free energy calculations using DFT shows that H₂, CO production occurs faster and is thermodynamically easier over dual active site TM-Mo₂C. Thus, novel reaction pathway of methane-assisted biomass reforming over bi-functional transition metal (Fe / Ni / Pd) and molybdenum carbide (Mo₂C) has been validated using experimental catalyst screening approach integrated with molecular thermodynamic calculations and kinetic modelling.

Figure 44 Production rate of $CO(g)$ and $H_2(g)$ during the methane assisted p-cresol reforming reaction over the pure and transition metal doped $Mo_2C(001)$ surfaces at temperature range 1073 K – 1273 K. Total pressure 1 bar, p-cresol: CH_4 in 1:1 ratio.

4.4 Comparison of methane assisted p-cresol, lignin, biomass reforming

Catalyst evaluation and molecular modelling investigation were in complete agreement with the earlier proposed reaction mechanism for methane assisted biomass reforming. Free energy diagram shown in Figure 39 illustrates that dual active sites are necessary for CH₄ activation and p-cresol HDO. It was observed that β -Mo₂C binds reactants and products very strongly and is quite capable of CH₄ activation and p-cresol HDO. However, adsorbed product species CO and H₂ are too stable on the surface to get desorbed in the gas phase as seen from the energy barrier on pure Mo₂C (Figure 38(d, e)). Compared to pure Mo₂C, TM-a-Mo₂C had slightly lower barriers for desorption of H₂ and CO. Especially, H₂ (1.15 eV, 1.13 eV) is easily desorbed on Fe-a-Mo₂C and Ni-a-Mo₂C compared to CO (2.87 eV, 2.80 eV) (Table 14). Thus, CH₄ assisted reforming studies were performed for complex feedstocks lignin and biomass which are comprised a wide array of oxygenates derivatives. Along with Fe-Mo₂C-GNS and Ni-Mo₂C-GNS, Pd-Mo₂C-GNS catalyst was also employed for these reactions. Comparison of Pd-Mo₂C-GNS was performed because of higher conversions achieved with addition of Pd to the Mo₂C-GNS catalyst. Pd-Mo₂C-GNS was also compared with Fe-Mo₂C-GNS and Ni-Mo₂C-GNS as higher gas yield (~38 mol.%) was obtained for CH₄-assisted p-cresol reforming.

Figure 45 shows comparison of syngas composition and conversion obtained from CH₄ assisted p-cresol, lignin, and biomass reforming. CH₄-lignin synergistic co-processing on Fe-Mo₂C-GNS catalyst showed highest concentration of H₂ in product gas with H₂:CO ratio of 3.88 and 99% conversion. H₂ based conversion was more than 90% on both lignin and biomass on Fe-Mo₂C-GNS. Reactions performed on Fe-Mo₂C-GNS and Ni-Mo₂C-GNS catalyst showed high HDO and H₂ based conversion for lignin and biomass (Figure 45). However, H₂:CO ratio decreased significantly from 3.84 with p-cresol to just 2.3 with lignin. H₂:CO ratio improved for CH₄ assisted biomass reforming to 2.73 compared to lignin on Ni-Mo₂C-GNS. Higher conversion with lignin and biomass is an indication of extensive HDO and steam methane reforming occurring with lignin and biomass feeds. On Ni-Mo₂C-GNS, CO desorption to gas phase was more favorable as seen from lower absorption energy values on Ni-Mo₂C-GNS (Figure 38(e)). CO was less stable on Ni-Mo₂C-GNS (-2.07 eV) compared to that on Fe-Mo₂C-GNS (-2.15 eV). H₂ stability was similar on both Ni-Mo₂C-GNS and Fe-Mo₂C-GNS (-1.13 eV and -1.15 eV respectively). Thus, HDO conversion was lower on Fe-Mo₂C-GNS (54%) than over Ni-Mo₂C-GNS (65%) for CH₄ – biomass reaction. Both HDO conversion and H₂ based conversion was much higher on Pd-Mo₂C-

GNS catalyst for reactions with all three feeds as predicted (Figure 45). However, $H_2:CO$ ratio obtained over Pd-Mo₂C-GNS catalyst was lowest among the three catalyst for biomass feed at 2.58. Based on $H_2:CO$ ratio in the syngas with biomass feed, the performance of these catalysts followed the order: Fe-Mo₂C-GNS > Ni-Mo₂C-GNS > Pd-Mo₂C-GNS. Following section explains why the choice of Fe-Mo₂C-GNS is highly suitable for synergistic flare gas – biomass co-processing reaction.

Figure 45 Comparison of CH₄ assisted reforming of p-cresol, lignin, and biomass over Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalysts. Reaction conditions: Temperature = 1073 K, Gas feed: 10 sccm CH₄, 190 sccm N₂

4.5 Comparative catalyst performance for methane assisted lignin and biomass reforming

Methane assisted lignin and biomass reforming performed over the three catalysts was compared based on syngas composition, conversion based on CO, CO₂ and H₂ in the feedstock and product gas (Table 15, Figure 46 in Supporting Information). Hydrogen rich syngas could be obtained on Fe-Mo₂C–GNS catalyst on both lignin and biomass with higher conversion compared to Ni/Pd-Mo₂C-GNS catalyzed reaction. Performance of Pd-Mo₂C-GNS catalyst was much worse on lignin and biomass in terms of hydrogen production compared to that of Fe/Ni-Mo₂C–GNS. Also, Pd being a noble and expensive metal, Pd-Mo₂C-GNS catalyst was not selected for comparative DFT modelling. Both Fe/Ni-Mo₂C–GNS are expected to perform equally well based on DFT modelling results. However, performance and resistance of Fe-Mo₂C–GNS catalyst was better for lignin and biomass reactions as evident by higher H₂:CO ratio with similar conversion on Fe-Mo₂C–GNS and Ni-Mo₂C-GNS catalysts. For CH₄ assisted reforming of lignin, H₂:CO for the reaction performed on Fe-Mo₂C–GNS was 3.88 compared to just 2.3 on Ni-Mo₂C-GNS. Similarly, for the biomass reaction on Fe-Mo₂C–GNS generated high H₂:CO of 3.22 compared to 2.73 on lignin. H₂ production for CH₄ assisted lignin reforming was nearly twice on Fe-Mo₂C–GNS compared to Ni-Mo₂C-GNS reaction. For both the feedstocks lignin and biomass, Ni/Pd-Mo₂C-GNS were not as suitable for production of hydrogen rich syngas as Fe-Mo₂C–GNS. This is in stark contrast to observations made in the case of p-cresol. Fe-Mo₂C–GNS performance was comparatively poor for CH₄ assisted p-cresol reforming. Major difference between p-cresol and lignin, biomass is in the elemental composition and molecular structure. Lignin and biomass also contain other types of oxygen bonds like R – O – R, benz – O – CH₃, RCOOR, RCOOH. Moreover, thermal cracking leads to higher degree of steam methane reforming and HDO on Fe-Mo₂C–GNS thus producing high H₂:CO with higher conversion. CO, CO₂ and H₂ based conversion was 99% on for methane – lignin reaction on Fe-Mo₂C–GNS. HDO conversion in methane assisted biomass reforming on Fe-Mo₂C–GNS was 91% and H₂ based conversion was 54% which was comparable to slightly higher conversion on Ni-Mo₂C-GNS: 90% HDO and 65% hydrogen-based conversion. CH₄ activation and steam adsorbates from HDO of biomass must interact with each other to successfully cause steam methane reforming. With high H₂:CO ratio for reaction on Fe-Mo₂C–GNS, good conversion, and highly dispersed Fe, Mo₂C crystals; Fe-Mo₂C–GNS is the obvious choice for synergistic flare gas – biomass co-processing.

Figure 46 a) Syngas composition for CH₄ activated gasification of lignin b) Syngas composition for CH₄ activated gasification of biomass. Catalysts: Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, Pd-Mo₂C-CNF. Reaction conditions: Temp = 800°C (1073 K), gas feed: 10 sccm CH₄, 190 sccm

Table 15 HDO and H₂ based conversion on Fe-Mo₂C-GNS, Ni-Mo₂C-GNS, and Pd-Mo₂C-GNS catalysts used in methane assisted reforming of p-cresol, lignin, and biomass

Feedstock with 5 mol.% CH₄	Catalyst Support: GNS	H₂:CO	HDO Conversion (%)	H₂ Based Conversion (%)
p-cresol	Fe-Mo ₂ C	2.37	72	34
	Ni-Mo ₂ C	3.84	81	24
	Pd-Mo ₂ C	3.50	82	70
Alkali lignin	Fe-Mo ₂ C	3.88	99	99
	Ni-Mo ₂ C	2.30	76	59
	Pd-Mo ₂ C	2.78	91	81
Hardwood biomass	Fe-Mo ₂ C	3.22	54	91
	Ni-Mo ₂ C	2.73	65	90
	Pd-Mo ₂ C	2.58	68	97

4.6 Stability and performance of Fe-Mo₂C-GNS catalyst for CH₄ assisted reforming of lignin and hardwood biomass

Figure 47 shows the HDO conversion of lignin and biomass along with H₂:CO ratio in the syngas for reactions performed on the Fe-Mo₂C-GNS catalyst at 800°C. Higher H₂:CO ratio was observed in lignin reforming along with higher total HDO conversion of ~95%. H₂:CO ratio in lignin was initially >4 with low CO and CO₂ concentration indicating slower HDO conversion. H₂:CO ratio decreased steadily between 20 to 55 min of reaction at 800°C. HDO conversion was less than 5% until 10 min into the reaction for lignin reforming. HDO conversion of lignin picked up after 10 min and continued to rise linearly until 65 min of isothermal reaction. Nearly zero conversion was observed at the start and end of isothermal lignin reforming at 800°C. However, total HDO conversion was well above 90% indicating excellent TOS performance of the Fe-Mo₂C-GNS catalyst. CH₄ assisted biomass reforming was similar to lignin reforming albeit with lower H₂:CO ratio since the start of the reaction. HDO conversion of biomass was ~88% at the end of the isothermal reforming reaction. Although biomass generated syngas comprised of higher CO concentration compared to the syngas from lignin, biomass contains 49 wt.% oxygen as compared

to only 30 wt.% in lignin. Thus, the HDO conversion in biomass falls slightly short of lignin. HDO reactions in biomass at a constant rate up to 65 minutes into the reaction.

CH₄ assisted reforming of both lignin and biomass shows excellent performance in the time-on-stream tests conducted over the Fe-Mo₂C-GNS catalyst. Extensive investigation of catalyst stability over 3 compositions of Fe-Mo₂C-GNS/CNF catalyst (Fe: 0.5, 2.5, 5 wt.%, Mo: 4 wt.%) were performed for CH₄-CO₂ assisted biomass reforming at temperatures of 800°C, 850°C, and 900°C. 15 reforming cycles were performed without requirement of external regeneration of the GNS / CNF based catalyst for time-on-stream (TOS) performance of 2 hours. Reforming cycles were performed over 3 catalyst compositions with Fe concentration of 0.5, 2.5, and 5 wt.% and Mo concentration of 4 wt.%. Reaction cycles were performed at 800°C, 850°C, and 900°C. A total of 75 reforming experiments were performed using 5 mol.% CH₄ and 1 mol.% CO₂ with hardwood biomass. CO₂ was added to the CH₄ feed for achieving better control over the syngas composition. Addition of CO₂ does not alter the reforming pathway of CH₄ activation and HDO reforming of biomass. CO₂ addition lead to dry reforming of hydrogen and reforming of amorphous coke / free-C on the surface to yield higher CO concentration in the syngas. Stable syngas composition and high H₂ based conversion and HDO conversion was obtained in the cyclic studies. In-situ regeneration of the Fe-Mo₂C-GNS / CNF catalyst was observed in 15 reforming cycles. In-situ regeneration phenomenon has been validated using extensive TEM imaging, XRD, Raman, and TGA characterization of the catalysts. Catalyst performance in the 15th cycle was at par with the performance in the first cycle.[133]

Figure 47 Hydrodeoxygenation (HDO) cumulative conversion and syngas composition ($H_2:CO$ molar ratio) obtained in CH_4 assisted reforming of lignin and hardwood biomass over Fe-Mo₂C-GNS catalyst

Crystalline coke deposition on the Fe/Ni-Mo₂C-GNS catalysts was observed from reactions performed for CH_4 assisted lignin reforming. Figure 48(a) shows CNT formation over Fe / Mo₂C active sites. Similarly, CNF growth was observed on the Ni-Mo₂C-GNS catalyst (Figure 48(b)). It was observed from time-on-stream and reforming cyclic studies that crystalline carbon growth on the active sites does not diminish the activity. Stable activity of TM doped Mo₂C catalyst was observed for CH_4 assisted p-cresol, lignin, and biomass reforming. Amorphous metal phase of Ni was observed in the Ni-Mo₂C-GNS catalyst after the reaction as shown in Figure 49.

a) CNT growth on spent Fe-Mo₂C-GNS

Crystalline coke content from TGA
weight loss at T > 500°C: 11.25 wt. %

b) CNT growth on spent Ni-Mo₂C-GNS

Crystalline coke content from TGA
weight loss at T > 500°C: 9.17 wt. %

Figure 48 Crystalline coke formation over Fe-Mo₂C-GNS (20 nm) and Ni-Mo₂C-GNS (50 nm) catalysts after being subjected to CH₄ assisted p-cresol reforming at 800°C (1073 K).

Figure 49 Amorphous metallic phase on the spent Ni-Mo₂C-GNS catalyst employed for CH₄ assisted p-cresol reforming at 800°C (1073 K). TEM image at 50 nm and high magnification image at 10 nm shows the amorphous Ni / Mo₂C dispersion.

4.7 Conclusions

A novel lignin and biomass reforming reaction pathway has been investigated in detail and the synergy of co-processing with flare gas has been validated through integrated molecular modelling approach coupled with experimental results. TM-Mo₂C-GNS was developed using inexpensive hardwood biomass as GNS support precursor. P-cresol, a model compound for lignin when co-processed with 5% CH₄ showed promising results both experimentally and through DFT modelling. Fe-Mo₂C-GNS and Ni-Mo₂C-GNS emerged as two suitable candidates for efficient catalytic co-processing. Dual active site theory and in-situ methane activation with HDO of p-cresol was validated based on theoretical and experimental investigation. Fe-a-Mo₂C-GNS and Ni-a-Mo₂C-GNS present low energy barrier for H₂ desorption into gas phase (1.15 eV, 1.13 eV) compared to strongly adsorbed H₂ on Mo₂C-GNS (-1.7 eV). CO desorption in gas phase was easier on Ni-a-Mo₂C-GNS (2.80 eV) compared to Fe-a-Mo₂C-GNS (2.87 eV) and Mo₂C-GNS (3.67 eV). This is also evident from high H₂:CO obtained in experiments on Fe-Mo₂C-GNS with lignin and

biomass (3.88, 3.22) compared to Ni-Mo₂C-GNS (2.3, 2.73). XRD measurements performed also showed distinct peaks for Ni in Ni-Mo₂C-GNS and β -Mo₂C confirming the presence of independent active sites. SEM-EDX elemental mapping of Fe-Mo₂C-GNS and Ni-Mo₂C-GNS showed well dispersed Fe/Ni, β -Mo₂C crystals in close proximity. Fe-Mo₂C-GNS catalyst showed excellent performance with HDO conversion of 99% for lignin and comparable 54% for biomass along with high H₂:CO ratio of 3.88 and 3.22 respectively. Higher H₂:CO ratio in syngas was explained based on micro-kinetic model (MKM) of the proposed reaction pathway. H₂ production rate is of same order of magnitude but 2 to 4 times that of CO over Fe-a-Mo₂C and Ni-a-Mo₂C catalysts. Thermodynamically less favored Fe-r-Mo₂C and Ni-r-Mo₂C sites are as ineffective as Mo₂C for hydrogen rich syngas generation. Compared to Ni-a-Mo₂C, Fe-a-Mo₂C emerges as better catalyst for lignin and biomass reforming. Fe-Mo₂C-GNS shows stable activity for time-on-stream CH₄ lignin and biomass reforming. Integrated experimental – DFT approach provides deeper insights into advantages of co-processing of natural gas / flare gas with biomass.

Chapter 5. Self-regeneration of Graphene / CNF Supported Fe – Mo₂C Through CH₄ – CO₂ Assisted Biomass Reforming

Figure 50 Schematic of cyclic in-situ regeneration of CNF / GNS supported Fe-Mo₂C catalyst for CH₄-CO₂ assisted biomass reforming

5.1 High temperature CH₄ – CO₂ activation over GNS / CNF supported catalyst

Fe / Fe₃C and β -Mo₂C nanoclusters on the GNS support in 0.5Fe and 2.5Fe catalyst and CNF support in 5Fe catalyst are highly active for high temperature CH₄ and CO₂ activation. CO₂ activation is thermodynamically favored by the presence of adsorbed hydrogen on the neighboring surface. Dry reforming using 12.5 vol.% CH₄ and 2.5 vol.% CO₂ (CH₄:CO₂ = 5) was performed in absence of biomass for investigating the effect of CH₄, CO₂ on the catalyst active sites. Such investigation also provides the baseline for understanding the reaction mechanism of synergistic CH₄-CO₂ assisted biomass reforming. Dry reforming using CH₄-CO₂ was performed over 0.5Fe, 2.5Fe catalysts at 850°C and 5Fe catalysts at 800, 850, and 900°C. Figure 51 and Figure 52 show the product composition obtained from dry reforming at 850°C over 0.5Fe, 2.5Fe, and 5Fe fresh catalysts. With continuous flow of 25 sccm CH₄ and 5 sccm of CO₂ through the catalyst bed, time-on-stream was 75 to 82 minutes. Stable methane decomposition was obtained over 2.5Fe with

constant methane conversion of 95.4% and CO₂ conversion of 99%. Almost all of the methane was converted to hydrogen over 2.5Fe at 850°C. Although, CO₂ conversion was ~99%, CO concentration was just 3%. CO generation could be the result of two competing reactions occurring due to CO₂ activation and excess hydrogen in the gas phase. Following reactions occur over the Fe-Mo₂C catalyst with CH₄-CO₂ reforming:

Interestingly, CH₄ conversion dropped rapidly to < 45% on 800-5Fe, < 40% on the 850-5Fe, and 70% on the 900-5Fe catalyst. Low methane conversion on the 5Fe catalyst could be attributed to carbon saturated Fe active sites. Since 5Fe catalyst have high concentration of CNF in the support, methane conversion to crystalline carbon growth and hydrogen is hindered compared to the 0.5Fe and 2.5Fe catalyst which have graphene support. Fe sites are easily exposed and available for methane activation in absence of biomass on the 0.5Fe and 2.5Fe catalyst. However, due to low concentration of Fe sites (0.5%) on the 0.5Fe catalyst, methane conversion drops to 55% after 80 minutes time-on-stream. Among 5Fe catalyst, the highest CH₄ conversion was observed on the 900-5Fe catalysts probably due to higher reaction temperature. In the presence of biomass however, proximity of absorbed biomass oxygenates drives methane dissociation as the hydrogen interacts with the adsorbed oxygen on the neighboring sites. Thus, 5Fe catalysts perform better for CH₄-CO₂ assisted biomass reforming compared to dry reforming in absence of biomass. Boudouard reaction which converts most of the CO₂ to CO using the free-C on the catalyst is also affected by the Fe concentration in the Fe-Mo₂C catalysts. CO₂ concentration over 5Fe catalysts is ~60 to 70% but >99% on the 0.5Fe and 2.5Fe catalysts. Low CH₄ conversion which leads to lower hydrogen presence in the proximity to CO₂ and less free-C over the surface may be the cause of lower CO₂ conversion over 5Fe catalysts.

Dry reforming studies in absence of biomass provides valuable insights on the activity of Fe / Fe₃C and Mo₂C sites and effect of catalyst support on CH₄ and CO₂ activation. Moreover, the study also conclusively showed that Fe-Mo₂C is highly active for low CO_x hydrogen production and essentially CO₂ negative H₂ and CO production.

Figure 51 High temperature CH_4 - CO_2 activation and baseline reforming composition without biomass over a) 0.5Fe, b) 2.5Fe, and c) 5Fe catalysts at temperature: 850°C

Figure 52 High temperature CH_4 - CO_2 activation and baseline reforming composition without biomass over 5Fe at different temperatures. a) 800-5Fe, b) 850-5Fe, c) 900-5Fe

5.2 Effect of changing the CH₄/CO₂ at different reaction temperatures for reforming of biomass over 5% Fe-4% Mo₂C catalyst

When the idea of simultaneous CH₄-CO₂ activation over Fe-Mo₂C catalysts was being implemented as a proof of concept for lignocellulosic biomass reforming, authors had tried CH₄/CO₂ ratio of 1, 3, and 5 over 5% Fe-4% Mo₂C catalyst. However, with stoichiometric ratio of CH₄-CO₂, the gaseous feed can undergo dry reforming at high temperatures. Besides, equimolar amount of CO₂ in the feed produces increased the amount of CO₂ in syngas. With CH₄/CO₂ ratio of 1 and 3, the H₂:CO ratio obtained at 850°C was just 0.96 and 1.3 respectively. CO₂ concentration > 1% in the gas feed produces higher concentration of both CO and CO₂ as some carbon monoxide undergoes water gas shift (CO shift) to produce hydrogen. However, in the CH₄-CO₂ assisted biomass reforming, majority of hydrogen production occurs through hydrodeoxygenation followed by methane reforming. Synergistic hydrogen rich syngas production involves overall reactions like methane activation, HDO, methane reforming, and CO₂ activation. High temperature methane dissociation occurs via catalytic dehydrogenation to form adsorbed H* species on the catalyst surface. CO₂ activation at high temperatures with abundant H* adsorbed species in the proximity occurs via intermediate formate ions (COOH**). Metastable formate ion intermediates are converted to CHO** and further to CO* and H₂* in equimolar proportion. CO₂ activation steps are shown in eq. 18, 19, and 20.

Stoichiometric ratio of CH₄ and CO₂ in the gas feed may lead to undesired reactions like Boudouard reaction with free-C on the surface at high temperatures. Thus, CH₄ / CO₂ ratio of 5:1 is optimum for producing hydrogen rich syngas through reforming of biomass.

5.3 CH₄ – CO₂ assisted biomass reforming reaction over 0.5Fe and 2.5Fe catalysts

Earlier, CH₄-CO₂ assisted biomass reforming was also performed and compared over Fe-Mo₂C-CNF and conventional zeolite supported Fe-Mo-ZSM-5 catalysts. This comparison has been discussed in detail in the previous study.[31,96] It was observed that that GNS / CNF supported

catalysts produce higher syngas moles with higher turnover frequency compared to zeolite supported catalyst. GNS / CNF support produces unique metal-metal carbide active sites. Mo_2C and Fe_3C were not observed in the ZSM-5 supported catalyst. Metal carbides are known to provide excellent resistance to amorphous coke formation and subsequent poisoning of active sites. Biomass reforming reactions were initially performed using 0.5Fe and 2.5Fe catalysts (adhering to the nomenclature mentioned in Table 6). Figure 53, Figure 54 show the product composition and $\text{H}_2:\text{CO}$ ratio obtained over 15 cycles over 0.5Fe and 2.5Fe catalysts respectively. On 0.5Fe catalysts, it can be observed that the $\text{H}_2:\text{CO}$ varies between 2.3 in first cycle to 5 in the 15th cycle. Variation in the $\text{H}_2:\text{CO}$ ratio is largely observed due to variation in the H_2 concentration in syngas while CO concentration varied only between 15% to 20% over most cycles. Interestingly, CH_4 concentration change was also in a narrow range of 15% to 25% except cycles 13, 14, and 15. Sharp increase in CH_4 concentration in last three cycles is paralleled with decrease in both H_2 and CO concentrations indicating lower HDO and hydrogen conversion. As observed in Figure 53, CH_4 , CO, and CO_2 concentrations do not change significantly whereas the H_2 concentration varies between 45% to 60% of the syngas. Conversions are defined in three ways viz. hydrogen-based, HDO conversion, and carbon-based conversion show large variations in the 15 cycles. Carbon conversion is generally low (< 30%) but HDO conversion varies between 10% to 85% on the 0.5Fe catalyst (Figure 53) while on the 2.5Fe catalyst HDO conversion ranges between 10% to 60% (Figure 54). Hydrogen conversion is generally >80% but also shows large variations, typically between 20% to 100% on both 0.5Fe and 2.5Fe catalysts. Higher hydrogen concentration (>50%) is observed in cyclic reactions on both catalysts thus indicating that hydrogen rich syngas production is favored on the Fe- Mo_2C -CNF catalysts. A sharp decrease in HDO and hydrogen-based conversion in cycle 9 of the 0.5Fe catalyst (Figure 53) and cycles 2-3 and 14 of the 2.5Fe catalyst (Figure 54) is a pattern observed in cyclic reforming reactions performed with all three Fe loadings between 0.5% to 5%. A steep drop in conversion and linear increase in the subsequent cycles as observed in Figure 53, Figure 54 indicate successful regeneration of the catalyst. XRD analysis of the 2.5Fe catalyst (Figure 55) show that Fe active sites undergo carbide formation and agglomerates of Fe_3C -Fe active sites exist after a few cycles of reaction. Figure 56 show the TEM images of catalyst samples from different cycles on the 0.5Fe and 2.5Fe catalysts. In Figure 56(e $\rightarrow$ h), grey and black color patterns in the nanoparticles observed in Figure 56(f, g) are possibly agglomerated Fe- Fe_3C nanoclusters. β - Mo_2C does not undergo phase change and is quite stable

(Figure 55 – XRD, Figure 56 – TEM). In the fresh 0.5Fe and 2.5Fe catalysts, secondary peaks of β -Mo₂C and primary Fe-Fe₃C peaks are not observed indicating highly dispersed nanoclusters on graphene sheets. Table 16 shows approximate particle sizes of β -Mo₂C, Fe-Fe₃C on different CNF supported catalysts as calculated from the Scherrer formula. β -Mo₂C particle size increases in fresh 0.5Fe to 0.5-C12 and similarly in fresh 2.5Fe to 2.5-C14 catalyst samples. β -Mo₂C peaks are much sharper in intermediate catalyst samples for example 0.5-C3, C5 and 2.5-C2-3, C10 at $\sim 39.8^\circ$. The intensity of major peaks like β -Mo₂C decreases in 0.5-C10 and 2.5-C14 because of amorphous coke deposition that occurs after the catalyst regeneration is complete. Initially, the graphene nanosheet support encapsulates the Fe⁰ active sites to form Fe₃C and Fe₃C_x ($x > 1$) active sites. Once the 3d orbitals in Fe are saturated with electron pairs from undercoordinated carbon atoms in the graphene neighborhood, free-C from the reaction and surrounding dangling C bonds undergo CNF growth from 0.5-C3 and 2.5-C2-3 to 0.5-C10 and 2.5-C14 respectively. Once the Fe₃C_x nucleation sites are saturated with CNF growth, amorphous coke deposition temporarily shields the active sites. This is also evident from low gas yield, HDO conversion 0.5-C10 and 2.5-C14. Gas yield and HDO conversion, which follow a close trend, dropped to $\sim 20\%$ in cycle 9 from $\sim 50\%$ in the previous cycle. Low HDO conversion and gas yield indicate less interaction between CH₄ and biomass thus leaving some oxygenates unconverted. Such transformation from graphene encapsulated CNF support to graphene layer formation in 2.5Fe catalysts is observed from the TEM images (Figure 56(e $\rightarrow$ h)). In the fresh 2.5Fe catalyst, about 60 to 70% of the carbon is graphene with small CNFs. After cycle 2-3 the support was completely observed as CNF shells with smaller thickness but larger shell diameters. Steep decrease in HDO conversion and gas yield in cycle 2-3 from $\sim 60\%$ to $\sim 15\%$ (Figure 54) is possibly due to nucleation or onset of regeneration. As such regeneration occurs gradually, conversion and gas yield increased back to original level and remained nearly constant with smaller drop in 10th cycle (Figure 55). In Figure 56(g), catalyst sample from 10th cycle show marked difference in the support structure.

Syngas composition on both 0.5Fe and 2.5Fe catalysts shows consistent hydrogen concentration of more than 40% and 50% respectively. H₂:CO ratio is higher in initial cycles performed on 2.5Fe catalysts compared to that on 0.5Fe catalysts. However, H₂:CO between 3 to 4 is observed in most of the later cycles performed on both the catalysts. CH₄, CO, and CO₂ concentration is below 30% for 15 cycles performed on both catalysts. Nucleation and growth of graphene cover over the 2.5Fe

CNF catalyst and similar CNF growth on the 0.5Fe catalysts play an important role in protecting the vital metal – metal carbide active sites for CH₄-CO₂ activation and reforming reactions.

Figure 53 Conversion and product composition of 5% CH₄ – 1% CO₂ assisted biomass reforming reactions performed in 15 cycles over 0.5% Fe – 4% Mo₂C at temperature: 850°C. Nomenclature: ‘C’#’: Cycle number 1 through 15

Figure 54 Conversion and product composition of 5% CH₄ – 1% CO₂ assisted biomass reforming reactions performed in 15 cycles over 2.5% Fe – 4% Mo₂C at temperature: 850°C. Nomenclature: ‘C’#’: Cycle number 1 through 15. Cycle 2-3 indicate that experimental data co could not be retrieved for second cycle due to technical fallout in the product analysis setup. Data obtained in cycle 3 is a combination of effect from cycle 2 and cycle 3. Therefore, it is indicated as C2-3.

Figure 55 XRD measurements pattern of 0.5% Fe-4% Mo₂C-CNF and 2.5% Fe-4% Mo₂C-CNF catalysts subjected to different cycles. ‘♣’: Graphitic carbon, ‘*’: β-Mo₂C, ‘♠’: Fe₃C, ‘◆’: Fe. All catalyst from different cycles were subjected to reaction temperature of 850°C.

Figure 56 TEM images of fresh 0.5% Fe – 4% Mo₂C-CNF catalyst and after selected cycles viz. 3rd, 5th, and 12th cycles subjected to CH₄ – CO₂ assisted biomass reforming at 850°C. TEM images obtained at 200 kV with beam current ~110 μ m. ‘0.5 / 2.5’ indicates iron loading of the catalyst, C# indicates spent catalyst from the specific cycle. a) 0.5Fe – Fresh at 50 nm b) 0.5 – C3 at 20 nm, c) 0.5 – C5 at 50 nm, d) 0.5 – C12 at 20 nm, e) 2.5Fe – Fresh at 50 nm f) 2.5 – C2/3 at 100 nm, g) 2.5 – C10 at 50 nm, h) 2.5 – C14 at 50 nm

Table 16 Approximate crystal sizes / thickness of CNF, β -Mo₂C, and Fe / Fe₃C on the Fe – Mo₂C – CNF catalyst with Fe loading of 0.5%, 2.5%, and 5% and Mo loading of 4%. Catalysts subjected to temperatures 800°C, 850°C, and 900°C

Catalyst	CNF thickness (nm)	β -Mo ₂ C (nm)	Fe / Fe ₃ C (nm)
5Fe-Fresh	3.37	22	5.38
5-C2 800°C	1.14	29.8	28
5-C11 800°C	1 to 4.5	30.61	4.9
5-C15 800°C	1.75 to 2.1	31	4.9
5-C2 850°C	1.1	38	36.5
5-C5 850°C	1	32.65	5
5-C9 850°C	0.92	37.36	4.4
5-C2 900°C	3.9	33.74	11 to 23.5
5-C6 900°C	1 to 6.77	31.58	6
5-C11 900°C	1.9 to 2.26	32.73	6
0.5Fe-Fresh	0.605	18.35	0.5
0.5-C3	0.9	32.12	0.61
0.5-C5	1 to 2.83	32.67	6.5
0.5-C12	0.9 to 21.67	41.32	4.22
2.5Fe-Fresh	0.62	22.64	0.9
2.5-C2/3	0.94 to 5.2	30.51	8.26
2.5-C10	1.1 to 3.7	31.27	4.5
2.5-C14	0.85 to 4.33	37	3.9

5.4 CH₄ – CO₂ assisted biomass reforming reaction over 5% Fe – 4% Mo₂C – CNF at reaction temperatures: 800°C, 850°C, and 900°C

The iron loading on the Mo₂C-CNF supported catalyst was increased from 0.5% and 2.5% to 5%. Higher Fe loading improves the quality and homogeneity of nanofibers in the CNF support and sustain the catalyst activity over 15 cycles. For detailed investigation of this hypothesis, CH₄-CO₂

assisted biomass reforming was performed at temperature of 800°C to 900°C. Comparative study of syngas composition, conversion, and CNF characterization over 15 cycles provides vital information for ascertaining the self-regenerable nature of the Fe-Mo₂C-CNF catalyst (Figure 57, Figure 58, Figure 59). Increasing the Fe loading on the CNF catalyst provides more accurate XRD measurements for size of Fe / Fe₃C nanoparticle (Figure 60). As seen in Figure 57 from reactions over 800-5Fe catalysts, H₂:CO ratio and hydrogen concentration increased significantly in cycle 3 and 4 and dropped steeply to yield a ratio of ~2 between cycles 6 to 10 and ~1.5 between cycles 10 to 15. Similarly, hydrogen concentration dropped from 67% in cycle 4 to ~40% for cycles 6 to 10. HDO conversion and gas yield dropped significantly in cycles 3 and 4 indicating methane decomposition and transformation of the CNF support. This is also evident from the decrease in CH₄ concentration in cycle 4. As seen in the TEM images and XRD measurements for the 800-5Fe catalyst, initial graphene-CNF structure changes to predominantly CNF shell structure with a sharp peak at 26.5°. The carbon peak around 26° broadens in 800 5-C11 and 800 5-C15 samples after 11th and 15th cycle. This indicates graphene formation over small CNF shells as evident from Figure 61(b → d). From XRD measurements in Figure 60, it can be observed that fresh 5Fe catalyst initially contains elemental Fe active sites which react with the undercoordinated carbon in the support and free carbon from the reaction to form Fe₃C sites after 2nd cycle with two distinct peaks appearing the XRD around 44° and 45°. Fe₃C and Fe peaks are also observed in the 800 5-C11 sample but only Fe₃C peak is distinctly observed in 800 5-C15 sample. Graphene nucleation probably began in the 11th cycle and continued until 15th cycle. From Figure 61(b, c), grey and pitch black colored shades are seen possibly indicating Fe-Fe₃C nanoparticles. Edges of the Fe nanoparticle are converted to Fe₃C over the 15 cycles as evident from XRD peaks. Conversion of Fe to Fe₃C nanoparticles along with lower temperature may present additional barrier for H₂ desorption in gas phase leading to low H₂:CO ratio and significantly lower hydrogen-based conversion over all 15 cycles compared to reactions performed at 850°C and 900°C. As reported in the previous study, Fe-Fe₃C active sites are responsible for CH₄ activation and Mo₂C for activation of the π ring in oxygenated aromatic species in biomass. In the presence of Fe, Mo₂C active sites facilitate hydrodeoxygenation and easier release of H₂, CO in syngas.[94] Over multiple cycles, Fe₃C active sites largely outnumber Fe sites which may lead to higher stabilization of product species on Fe₃C. Moreover, it has been reported that Fe sites are converted to Fe₃C and Fe₃C_x due to large amount of free-C from coke. Once metastable Fe₃C_x active sites are formed,

they serve as the nucleation point for formation of graphene. Graphene cover nucleation on metastable Fe_3C and Fe_3C_x continues with increasing number of reaction cycles. This kind of rearrangement is observed in catalyst samples from reactions performed at 800°C, 850°C, and 900°C especially in 5Fe catalysts over 15 cycles. In Figure 62 the rearrangement of CNF support and growth of graphene layer over CNF shells is clearly observable in spent catalysts with higher number of cycles. In contrast, the change in graphene support was very low in 0.5Fe catalyst samples (Figure 56). Graphite / graphene layers in 0.5Fe cycles did not undergo complete transformation to achieve CNF growth. In 2.5Fe cycles, the effect of $\text{Fe} \rightarrow \text{Fe}_3\text{C}$ is more pronounced. 2D graphene layer in the fresh catalyst underwent rapid transformation and growth to CNF in 2.5-C2/3 (Figure 56(e $\rightarrow$ h)). CNF / CNT growth is known to occur rapidly on elemental Fe sites in graphene framework after being rapidly converted to Fe_3C / Fe_3C_x . Fe_3C and Fe_3C_x being metastable in nature react at high temperature to form elemental Fe and free-C. Free-C is involved in the rearrangement to CNF.[134]

Conversion and syngas composition for cycles performed over 850-5Fe catalysts are shown in Figure 58. As compared to reactions performed on 0.5Fe, 2.5Fe, 800-5Fe, and 900-5Fe, conversion, gas yield, and syngas composition did not undergo sharp reduction or increase in specific cycles. Conversion, gas yield, and syngas composition was closer to average over 15 cycles. XRD analysis showed in Figure 60 for 850-5Fe, peaks for $\beta\text{-Mo}_2\text{C}$ and Fe / Fe_3C were distinguishable in all specific samples from fresh to highest spent catalyst. Interestingly, TEM images of 850-5Fe catalysts as seen in Figure 61(e $\rightarrow$ h) shows that CNF support did undergo significant rearrangement, graphene layering, and reduction in CNF size in sample from 2nd cycle (Figure 61(f)), 5th cycle (Figure 61(g)), and 9th cycle (Figure 61(h)) compared to the support in fresh catalyst (Figure 61(e)). Layer of graphene over small carbon nanofiber shells is clearly observed in Figure 62(c, d). However, more balanced performance of 850-5Fe over 15 cycles is surprising compared to reactions performed at lower (800°C) and higher temperatures (900°C). HDO conversion and gas yield from 850-5Fe cycles did not drop below 30% over 15 cycles as compared to 20% or below in reactions performed on other catalysts at 800°C to 900°C. Hydrogen-based conversion was 40% or higher in all 15 cycles with average gas yield of 40%. Hydrogen concentration in the syngas steadily increased over 15 cycles with intermittent drop in 5th and 13th cycle (Figure 58). CH_4 and CO concentration undergo little variations. However, rise in CH_4 concentration is generally accompanied by equivalent drop in CO concentration owing to the HDO

reforming effect (Figure 58). Successful HDO reforming of biomass should indirectly convert CH_4 to CO and CO_2 . In cycle 5, both CH_4 and CO concentration are equal and generally higher. Hydrogen concentration drops to a low of $< 30\%$ in cycle 5. However, at the same time HDO conversion is rather high $\sim 70\%$. This indicates higher HDO reforming dominating other hydrogen producing reactions like high temperature water gas shift and catalytic methane decomposition. Although CO_2 concentration varies the least between 10% to 15% over all cycles, CO_2 is essential for promoting further reforming of biomass through dry reforming of hydrogen. This helps to balance high hydrogen concentration by producing more CO . $\text{H}_2:\text{CO}$ ratio over all 15 cycles was close to an average of 2 in Figure 58 with exceptions in cycles 5, 11, and 14.

Figure 57 Conversion and product composition of 5% CH₄ – 1% CO₂ assisted biomass reforming reactions performed in 15 cycles over 5% Fe – 4% Mo₂C at temperature: 800°C. Nomenclature: ‘C’#: Cycle number 1 through 15

Figure 58 Conversion and product composition of 5% CH₄ – 1% CO₂ assisted biomass reforming reactions performed in 15 cycles over 850-5Fe catalyst at temperature of 850°C.
Nomenclature: ‘C’#’: Cycle number 1 through 15

Reactions performed on 900-5Fe catalyst samples are shown in the form of conversion and syngas composition in Figure 59. Similar to 0.5Fe, 2.5Fe, and 800-5Fe cycles, 900-5Fe cyclic reactions showed significant drop in hydrogen-based conversion, HDO conversion, and gas yield in 3 interval cycles: 2nd, 11th, and 12th. HDO conversion and gas yield which follow close trend dropped to 40% and 25% respectively in 2nd cycle and to ~20% in 11th – 12th cycles. Hydrogen-based conversion also dropped to ~35% in the 2nd, 11th, and 12th cycle. Carbon conversion remained low (~15%) in all the cycles with smaller variations. H₂ concentration remained high (~55%) in most of the cyclic reactions (Figure 59). Interestingly, average CH₄ concentration was similar to CO₂ concentration in all cycles, which is lower than average of 25% to 30% observed in other cyclic reactions. In contrast, average CO concentration was slightly higher (>25%) for most of the cycles. Lower CH₄ concentration and higher CO concentration is an indication of better HDO reforming in reactions performed on 900-5Fe catalysts. Thus, the H₂:CO was between 2 and 2.5 for most of the cycles, which is ideal for downstream chemical synthesis. 900-5Fe cyclic reaction system provided better syngas composition along with conversion compared to other reaction systems. XRD measurements from Figure 60 clearly show peaks for Fe / Fe₃C and Mo₂C in all samples from specific cycles. XRD measurements on 900 5-C11 showed predominantly Fe₃C with small Fe nanoclusters after 11 cycles. β -Mo₂C remained unchanged over all 15 cycles. Changing composition of Fe / Fe₃C active sites greatly affect the conversion, gas yield, and syngas composition in the 900-5Fe cyclic tests. TEM images in Figure 61(i, j) shows larger size CNF / CNTs present in fresh 5Fe catalyst and 900 5-C2 respectively. Graphene layering is observed in Figure 61(k, l) in 900 5-C6 and 900 5-C11 spent samples. Following section explains possible regeneration mechanism in spent catalysts from different cycles subjected to reaction at different temperatures.

Figure 59 Conversion and product composition of 5% CH₄ – 1% CO₂ assisted biomass reforming reactions performed in 15 cycles over 5% Fe – 4% Mo₂C at temperature: 900°C. Nomenclature: ‘C’#: Cycle number 1 through 15

Figure 60 XRD measurements pattern of 5% Fe-4% Mo₂C-CNF catalysts subjected to different cycles at reaction temperatures of 800°C, 850°C, and 900°C. ‘♣’: Graphitic carbon, ‘*’: β-Mo₂C, ‘♠’: Fe₃C, ‘♦’: Fe.

Figure 61 TEM images of fresh 5% Fe – 4% Mo₂C-CNF catalyst and after selected cycles subjected to CH₄ – CO₂ assisted biomass reforming at 800°C, 850°C, and 900°C. TEM images obtained at 200 kV with beam current ~110 μ m. Temperature mentioned in caption is reaction temperature, ‘5Fe / 5’ indicates iron loading of the catalyst, C# indicates spent catalyst from the specific cycle. a) 5Fe – Fresh at 100 nm b) 800 5 – C2 at 100 nm, c) 800 5 – C11 at 100 nm, d) 800 5 – C15 at 100 nm, e) 5Fe-Fresh at 50 nm, f) 850 5-C2 at 50 nm, g) 850 5-C5 at 100 nm, h) 850 5-C9 at 100 nm, i) 5Fe-Fresh at 50 nm, j) 900 5-C2 at 100 nm, k) 900 5-C6 at 100 nm, l) 900 5-C11 at 100 nm

Figure 62 TEM images show changes in nature of CNF support of 5% Fe – 4% Mo₂C catalysts subjected to reaction temperatures of 800°C, 850°C, and 900°C. Progression of cycles show CNF shells being reduced in size and undergo gradual coverage of graphene layer in samples analyzed after specific cycles. Nomenclature example: ‘800°C 5-C2’ indicates sample from 2nd cycle of CH₄-CO₂ activated biomass reforming reaction at 800°C performed over 5% Fe – 4% Mo₂C-CNF.

5.5 Comparison of catalyst performance in extensive CH₄ – CO₂ assisted biomass reforming

Comparative catalyst performance for CH₄-CO₂ assisted biomass reforming over 15 cycles was measured against an important metrics – Turn-over-frequency (TOF). TOF for each catalyst was calculated for each of the 15 cycles and averaged to yield overall performance of 0.5Fe, 2.5Fe, and 5Fe catalysts. Since 5Fe catalysts were subjected to reaction temperatures of 800°C, 850°C, and 900°C, average TOF varied between 0.21 to 0.24. However, 850-5Fe catalyst showed least variation in TOF over 15 cycles with a standard deviation of 12.1%. This indicates a more stable performance in terms of syngas composition, molar yield of syngas species, and conversion. Figure 58 shows the conversions and syngas composition obtained in 15 cycles of reaction over 850-5Fe catalyst. TOF was calculated based on syngas moles obtained in each reaction cycle. Since gas yield, HDO, hydrogen, and carbon conversion was more stable over 850-5Fe catalyst, TOF showed the least standard deviation (0.12) over 15 cycles compared to TOFs calculated for other catalysts. Generally, TOF varied by ~30% for 0.5Fe, 2.5Fe, 800-5Fe, and 900-5Fe catalysts. TOF calculation and % standard deviation for each catalyst is showed in Table 17. Based on the TOF calculations, it can be concluded that 5Fe catalyst subjected to reaction cycles at 850°C (850-5Fe) showed the best performance in terms of syngas composition and HDO conversion.

Table 17 Turnover frequency (TOF) averaged over 15 reaction cycles and % standard deviation in TOF for 0.5Fe, 2.5Fe, 800-5Fe, 850-5Fe, and 900-5Fe catalysts

Catalyst	Turnover Frequency (TOF)	
	Average (absolute value) (syngas moles g-catalyst ⁻¹ hr ⁻¹)	% Standard deviation
0.5Fe	0.2515	30.1
2.5Fe	0.2613	31.3
800-5Fe	0.2095	32.9
850-5Fe	0.2427	12.1
900-5Fe	0.2209	29.5

5.6 Stability of Fe-Mo₂C-CNF / GNS catalysts for extensive CH₄-CO₂ assisted biomass reforming

Fe-Mo₂C supported on GNS and CNF are stable dual-active site catalytic systems even after being subjected to 15 cycles of CH₄-CO₂ assisted biomass reforming at high temperatures ranging from 800°C to 900°C. Each cycle involved heating the catalyst bed at 10°C min⁻¹ and subsequent cooling to room temperature. The catalysts were removed from the reactor, weighed, and loaded in the packed bed without any ex-situ regeneration. Physical properties of the catalyst like density and particle size distribution were largely unchanged after 15 reforming reaction cycles. Temperature programmed oxidation (TPO / TGA) studies performed for 0.5Fe, 2.5Fe, and 5Fe catalysts under 2% O₂ – 98% He atmosphere up to 850°C showed an average weight loss of 40-50% in the fresh catalysts and 15-30% in the spent catalysts from different reaction cycles. This shows that the amount of impurities or free-C present in the fresh catalysts was much higher (2-3 times) compared to the spent catalysts. Crystallinity of the sp² hybridized carbon in the form of graphene / CNF improved after initial reaction cycles. Catalyst support thus became more stable and temperature resistant after being subjected to first few cycles. Particle size distribution and mean particle size of metal-metal carbide active sites was calculated for all catalyst samples selected for characterization from specific cycles. Table 18 shows the mean particle size and change in particle size over the course of 15 reaction cycles. For reaction cycles on all the catalysts at different temperatures, particle size distribution became flatter in the samples derived from later reaction cycles. Except the 2.5Fe cycles, particle sizes were more evenly distributed after 2nd cycle. This shows that the active sites on CNF / GNS support are quite stable and do not agglomerate into large clusters when continuously subjected to higher reaction temperatures. In-situ regeneration also renders more even particle size distribution in the Fe-Mo₂C-CNG/GNS catalysts.

Table 18 Mean particle size and % change in particle size relative to that in the fresh catalyst for 0.5Fe, 2.5Fe, and 5Fe catalyst samples specifically selected from reaction cycles.

Catalyst sample	Mean particle size (nm)	% change relative to fresh catalyst	95% Confidence Interval (Normal)
0.5Fe-Fresh	19.26		19.3 ± 6
0.5-C3	9.63	-50	9.6 ± 1.7
0.5-C5	9.14	-52.5	9.1 ± 1.5
0.5-C12	24.23	25.8	24.2 ± 9
2.5Fe-Fresh	17.62		17.6 ± 2.7
2.5-C2/3	13.65	-22.5	13.7 ± 2.8
2.5-C10	14.47	-17.9	14.5 ± 6.4
2.5-C14	14.5	-17.7	14.5 ± 5.2
5Fe-Fresh	17.16		17.2 ± 2.7
800 5-C2	25.1	46.3	25.1 ± 4.8
800 5-C11	17.89	4.3	17.9 ± 4.4
800 5-C15	12.93	-24.6	12.9 ± 2.3
850 5-C2	24.34	41.8	24.3 ± 4.7
850 5-C5	22.22	29.5	22.2 ± 4.4
850 5-C9	36.44	112.4	36.4 ± 8.6
900 5-C2	12.87	-25	12.9 ± 3
900 5-C6	28.19	64.3	28.2 ± 4.7
900 5-C11	34.68	102.1	34.7 ± 8.5

It is evident from Table 18 that Fe / Fe₃C – Mo₂C active sites are present as nanoclusters and small nanoparticles between average size of 9 to 36 nm. 95% confidence interval was also calculated to indicate the range of dispersed nanoparticle active species viz. Fe, Fe₃C, and Mo₂C

on the GNS / CNF support. Normal distribution of particle size was observed on all catalyst samples without large variation in the particle size. CI was typically around 20 to 25% indicating that 95% of the active nanoparticles were within 25% of the mean particle size calculated. Based on crystal size measurements calculated from Scherrer formula and XRD measurements indicated in Table 16 Mo₂C particles were larger in size compared to Fe and Fe₃C particles. Fe particles were smallest in size and probably existed as atomic nanoclusters than larger nanoparticles.

5.7 Self-regeneration mechanism of Fe / Fe₃C – Mo₂C catalysts supported over GNS / CNF (Discussion and proposed mechanism)

Figure 61, Figure 62 shows TEM images from catalysts imaged after specific cycles from CH₄-CO₂ assisted biomass reforming reaction performed at 800°C, 850°C, and 900°C. Common pattern is observed in the rearrangement and changes in CNF support with increasing number of reaction cycles. Graphene coverage begins to appear over the 5Fe catalysts typically after 5 to 6 cycles. Spent catalyst after 2nd cycle at all three temperatures clearly shows CNF shells and CNTs of varying thickness. Small CNF shells are visible in 800 5-C2 sample whereas CNT type structures are visible in 850 C-2 and 900 C-2 samples. The CNF / CNT support undergoes drastic transformation with graphene layer formed over possibly single walled CNF shells underlying the 2D layer. β -Mo₂C and Fe / Fe₃C sites are initially saturated and encapsulated with undercoordinated carbon in the support. However, β -Mo₂C is highly stable during the reaction conditions and does not undergo change in phase or composition. Defect induced graphene coverage is achieved over the underlying Fe₃C_x ($x > 1$) nanocluster embedded in CNF / CNT which could play vital role in altering the reaction environment while simultaneously protecting metallic / metal carbide active sites from harsh reaction environment. Graphene 2D cover over underlying saturated metastable Fe₃C_x provides quantum confinement effect thus reducing the chemical reactivity of underlying active species.[135–137] Reduced reactivity leads to optimization of the adsorption energies of small reacting species such as CH₄, CO, CO₂, and H₂. Graphene coverage was also shown to protect the active sites and prevent catalyst deactivation from harsh operating conditions. [138] Bao et al compared CO intercalation in graphene layered Pt(111) surface. It was observed that CO adsorption was weakened due to graphene layered Pt(111) compared to that on free Pt surface. Weakening of CO adsorption on Pt due to graphene prevents rapid CO poisoning

of the Pt active sites. It was reported that graphene layer not only lowers CO adsorption energy but also weakens the C-O bond.[139] Graphene layered catalyst thus produces nanoreactors for small reacting species by modulating their adsorption, desorption, and bond strengths. However, graphene layer over underlying active sites and support is only up to a height of 3 Å or 0.3 nm.[137] Thus larger molecules like lignin oxygenates face difficulty in adsorbing to the underlying active sites. Although this could lower the reforming conversion, gas yield, and significantly alter the syngas composition, graphene cover synthesis on the CNF supported catalyst is often imperfect and does not occur over the stable β -Mo₂C. Selective nucleation and growth of graphene sheets occurs mostly over the carbon saturated Fe₃C_x. 5Fe catalysts provides enough undercoordinated carbon surrounding Fe₃C_x growth sites for extensive graphene growth. Another major contribution to graphene coverage is the abundance of free-carbon in the form of coke generated from reforming and methane decomposition reaction. Graphene is also known to contribute as a catalyst itself by ‘dangling bonds’ effect generated from defects in graphene.[138] Surrounding graphene layer may reduce the bond strength of *O-C from lignin oxygenates due to availability of undercoordinated dangling carbon atoms in the neighborhood. Such qualitative analysis is based on evidences from studies performed for investigation of graphene promoted catalysts. Therefore, graphene layer formation on CNF supported 5% Fe – 4% Mo₂C observed over progression of cyclic reaction may have a stabilizing effect on the catalyst and delay catalyst deactivation. This is certainly evident from similar HDO conversion, gas yield, and syngas composition obtained in most of the cycles. Figure 63 shows schematic of in-situ regeneration occurring on the 5% Fe – 4% Mo₂C – CNF catalysts.

In contrast to the graphene layer formation on 2.5Fe (not shown here) and 5Fe (Figure 61, Figure 62) catalysts, graphene layer over CNF acts as the catalyst support in 0.5Fe catalysts as seen in the TEM images (Figure 56). Graphene as a catalyst support has also been extensively studied and widely reported. It was reported that transition metal adsorption on graphene occurs covalently due to strong hybridization of transition metal electronic states.[137,140–144] However, graphene adsorbed transition metals are weaker on pristine graphene surface and tend to mobilize to larger clusters and agglomerates. Vacancy enhanced graphene is more reactive towards stabilizing the metal adsorbates and preventing cluster formation. In Figure 56 (TEM images of 0.5Fe and 2.5Fe catalysts), much smaller nanoclusters of Fe / Fe₃C are formed on the graphene support. Underlying core CNF support in 2.5Fe catalysts possibly creates vacancies in the graphene layer.

Undercoordinated σ bonds and π bonds of the neighboring carbon atoms are called dangling bonds. These dangling bonds increase the reactivity of graphene toward metal / metal carbide adsorbates thus stabilizing them. Stabilization of metal nanoparticles and nanoclusters reduces their mobility during the reaction and also the diffusion barrier[137,139,145]. Figure 63 shows the schematic of in-situ regeneration of 0.5% Fe – 4% Mo₂C – GNS catalysts.

Figure 63 Proposed in-situ self-regeneration mechanism for a) 0.5Fe and 2.5Fe catalysts, b) 5Fe catalysts

5.7.1 Proposed in-situ regeneration mechanism on 0.5Fe, 2.5Fe, and 5Fe catalysts

In addition to the regeneration mechanisms described for the CNF / graphene support, metallic Fe active sites undergo conversion to Fe₃C and possibly Fe₃C_{1.5} (Fe₃C_x). In almost all of the fresh catalysts mentioned in this study (0.5Fe, 2.5Fe, and 5Fe), Fe active sites exist as a mixture of concentrated Fe⁰ and few Fe₃C nanoclusters. This is apparent from the weak to strong XRD peaks obtained at ~44.8°. However, as the reaction cycles progress to higher number, most of the Fe⁰ active sites are converted to Fe₃C and Fe₃C_{1.5}. Formation of stabilized Fe₃C_{1.5} can occur on the CNF / graphene support due to abundance of undercoordinated carbons. Although Fe₃C is considered as metastable and can revert to Fe, Fe₃C_x nanoclusters encapsulated by graphitic / graphene carbon are predominantly present especially in samples from cycles 5, 6 and higher. β -

Mo₂C nanoparticles (~30 nm) were very stable on the CNF supported catalysts and no phase change or mixture was observed in progression of the reaction over 15 cycles. Mo₂C nanoparticles tend to agglomerate and form larger particles with increasing reaction cycles. Following reaction mechanism has been proposed for regeneration and conversion of Fe active sites eq(21 → 28):

5.7.2 Thermogravimetry and raman spectroscopy evidence of catalyst stability and regeneration

Self-regeneration mechanism proposed above was clearly observed from thermogravimetry analysis of CNF supported catalyst oxidation (2 vol.% O₂, 98 vol.% He). In 0.5Fe, 2.5Fe, and 5Fe catalysts, 40% to 60% weight loss was observed in the fresh catalyst oxidation. This could be loose carbon, ash, char present on the catalyst from pyrolysis synthesis. Catalyst samples from successive cycles showed much lesser weight loss (10% to 30%). Exceptionally, 80% weight loss was observed on 2.5-C14 catalyst sample (Figure 64) which was surprising since other catalyst samples from similar cycles did not show such high loss in weight. Weight loss in fresh and spent catalyst was the least in 0.5Fe probably due to much high resistant graphene layer support (Figure 64). Typically, oxidation tests in catalyst from cycles 5 and above showed <20% weight loss (Figure 65, Figure 66, Figure 67). This indicates graphene layer formation over the CNF support providing higher resistance to oxidation. Raman spectroscopy measurements also support the

regeneration theory mentioned above. From Figure 68, in most of the Raman spectra, I_D/I_G ratio (ratio of peak intensity of d-band for disordered C or defects to peak intensity of g-band for graphitic carbon) increases in samples from successive cycles. 2.5Fe-Fresh and 5Fe-Fresh had the lowest I_D/I_G ratios of 0.77 and 0.76 respectively indicating lesser defects (Figure 68(a)). Interestingly, 2.5Fe-Fresh had initial support of graphene while 5Fe-Fresh had initial support of CNF / CNTs. 0.5Fe-Fresh meanwhile had I_D/I_G ratio of 0.85 which decreased to 0.77 in 0.5-C5 sample indicating much lesser defects in graphene support. However, in 0.5-C12, the I_D/I_G ratio increased to 0.85 possibly due to CNF growth generating more defects (Figure 68(b)). In the 2.5Fe samples, I_D/I_G ratio generally increased with disruptive CNF growth in pristine graphene layers and reached high of 0.88 in 2.5-C14 (Figure 68(c)). Figure 69(a) shows that I_D/I_G ratio increased sharply in 800 5-C2 to 0.91 and decreased after 11 cycles to 0.78. This sharp increase could be due to nucleation of graphene layer formation on carbon saturated Fe_3C_x active sites. After 11 cycles, graphene layer coverage was observed to a large extent from TEM images as well (Figure 61(c,d)). In Figure 69(b), I_D/I_G ratio sharply increased from 0.76 in 5Fe-Fresh to 0.96 in 850 5-C2. Interestingly, graphene layer was observed to a great extent already in 850 5-C2 sample from TEM image (Figure 61(f)). I_D/I_G ratio decreased marginally to 0.91 in 850 5-C9 after 9 cycles. This can be due to creation of defect in the form of vacancies in the graphene layer or growth of new CNFs. In Figure 69(c), I_D/I_G actually decreased initially to 0.74 in 900 5-C2, then increased to 0.86 in 900 5-C6 and further to 0.97 in 900 5-C11. I_D/I_G ratio could have decreased in the second cycle due to purification of the CNF / CNTs in the support as seen from clear TEM images in Figure 61(i, j). Graphene layer formation occurred by completion of cycle 6 which could have increased defects. 900 5-C11 had the greatest degree of defects or disordered C than in any samples which is evident from highest I_D/I_G ratio of 0.97. Raman spectra in Figure 68 and Figure 69 show that with graphene layer formation, amount of defects or disordered C content increases. Figures from TGA and Raman analysis are shown in supplementary information to limit the content of the article.

5.7.3 Surface area and pore volume investigation of catalysts

BET and BJH characterization of 5Fe catalysts subjected to reforming reactions at 800, 850, and 900°C is shown in Table 19. BET calculated surface area of 5Fe-Fresh catalyst was 167 m²/g. Specific surface area of the spent catalysts from different cycles decreased initially in the first few cycles and increased slightly as the catalyst support was regenerated. This trend is observed in 800-5Fe, 850-5Fe, and 900-5Fe samples consistently. Average pore width having the maximum

N₂ adsorption and desorption at -196°C (77K) was 3.5 nm in the 5Fe-Fresh catalyst and between 3.2 to 4.1 in the fresh and spent catalysts from different cycles. Interestingly, pore width increased initially in the 850 5-C2, 800 5-C2, and 900 5-C2 catalysts. Pore width was the lowest in the 9th to 11th cycle between 3.2 to 3.4 nm. However, catalyst samples analyzed from the 15th cycle showed slight increase in the pore width. Pore width increased to 3.4 nm in 800 5-C15 and 850 5-C15 catalysts whereas the pore width from 900 5-C15 catalyst was 3.6 nm, higher than that observed in the fresh catalyst. Total pore volume obtained at p/p⁰ of 0.99 showed interesting variations from fresh 5Fe catalyst to the catalyst sample obtained from 15th cycle. Due to the existence of small CNF shells in most of the catalyst samples, pore volume was generally low in the CNFs ranging from 0.018 to 0.27 cm³/g. Pore volume in the catalyst samples from 2nd cycle (5-C2) subjected to different reaction temperatures was 6 to 9 times higher than that in the fresh catalyst and samples subjected to higher number of reforming cycles. This multifold increase in total pore volume observed only in the 2nd cycle can be explained when coupled with TEM images and XRD results. As seen in the XRD results for 800, 850, 900 5-C2 catalysts in Figure 60, all the XRD peaks were distinctly observed with relatively much higher intensities compared to the XRD spectra of other samples. Compared to the 5Fe-Fresh catalyst, XRD peaks were sharp and distinct in the spent catalysts from 2nd cycle. Similarly, from the TEM images in Figure 61(b, f, j), catalyst support in the 5-C2 samples is much cleaner with pristine CNF / CNT structures compared to the fresh and other spent catalysts. When subjected to the reforming reactions, catalyst support undergoes regeneration through the evolution of Fe₃C_x species on the catalyst support. In the first 2 reforming cycles, the amount of loose carbon / free-C decreases substantially. This is also confirmed by the TGA-TPO results presented in supplementary information – Figure 65, Figure 66, Figure 67. Amount of free-C in the fresh catalyst was 40-50 wt.% and only between 20-30 wt.% in the 5-C2 catalysts. In the first two reforming cycles, free-C decreases to almost half of that in the fresh catalyst. When interlinked with the BET-BJH analysis of the samples, multifold increase in total pore volume is due to the opening of the pores at one end earlier clogged by the presence of loose-C. None of the pores however were open at both ends according the BJH adsorption-desorption results. Decrease in pore volume after the 2nd cycle was also high leading to total pore volume between 0.018 to 0.043 cm³/g. Although, the amount of free-C was less than 20 wt.% in the catalyst samples from later reforming cycles, formation of graphene layer over the CNFs may decrease the

pore volume substantially. After 15 reforming cycles, the catalyst support is regenerated with BET surface area, pore size, and total pore volume similar to that in the fresh 5Fe catalysts.

BET-BJH analysis for specific surface area, pore volume, and pore size clearly shows the in-situ regeneration of the support over 15 reforming cycles.

Table 19 N₂-adsorption characterization of 800-5Fe, 850-5Fe, and 900-5Fe catalysts from biomass reforming cycles

Catalyst	Specific surface area (m² g⁻¹)	Pore Width (nm)	Pore Volume (cumulative) (cm³ g⁻¹)
5Fe-Fresh	167	3.5	0.03
850 5-C2	134	4.1	0.27
850 5-C9	103	3.4	0.04
850 5-C15	131	3.4	0.036
800 5-C2	160	3.7	0.2
800 5-C11	17.7	3.2	0.018
800 5-C15	123	3.4	0.024
900 5-C2	121	3.8	0.18
900 5-C11	84	3.3	0.035
900 5-C15	115	3.6	0.043

Figure 64 TGA oxidation tests on 0.5Fe and 2.5Fe catalysts from ambient to 850°C under following gas composition: 2% O₂ – 98% He (100 sccm total flow).

Figure 65 TGA oxidation tests on 800-5Fe catalysts from ambient to 850°C under following gas composition: 2% O₂ – 98% He (100 sccm total flow).

Figure 66 TGA oxidation tests on 850-5Fe catalysts from ambient to 850°C under following gas composition: 2% O₂ – 98% He (100 sccm total flow).

Figure 67 TGA oxidation tests on 900-5Fe catalysts from ambient to 850°C under following gas composition: 2% O₂ – 98% He (100 sccm total flow).

Figure 68 Raman spectroscopy measurements for a) fresh 0.5Fe, 2.5Fe, and 5Fe catalysts b) 0.5Fe catalysts, and c) 2.5Fe catalysts

Figure 69 Raman spectroscopy measurements for a) 800-5Fe catalysts b) 850-5Fe catalysts, and c) 900-5Fe catalysts

5.8 Conclusions

Fe-Mo₂C-CNF supported catalysts undergo 15 self-regeneration cycles of CH₄-CO₂ activated biomass reforming reactions at temperatures ranging from 800°C to 900°C. Following conclusions were drawn from extensive investigation of Fe-Mo₂C-CNF catalysts for CH₄-CO₂ assisted biomass reforming:

- Dry reforming of CH₄-CO₂ in 5:1 ratio over 0.5Fe, 2.5Fe, and 5Fe catalysts showed that Fe-Fe₃C and Mo₂C activated CH₄ and CO₂ favorably at higher temperatures
- Hydrogen rich syngas composition can be obtained in all the reforming cycles and is largely unaffected by the onset or saturation self-regeneration occurring in 2 of the 15 reforming cycles.
- Average HDO conversion and gas yield of 45-50% shows that ligno-cellulosic biomass can be largely converted to hydrogen rich syngas through addition of external CH₄ and CO₂
- Correlation of catalytic performance and characterization shows that two distinct active centers are responsible for simultaneous methane – carbon dioxide activation and hydrodeoxygenation of oxygenates in lignocellulosic hardwood biomass.
- β -Mo₂C does not change in phase or composition over 15 cycles as evident from the XRD measurements.
- Low concentration loading of Fe leads to initial synthesis of graphene nanosheets (GNS) support in 0.5Fe and 2.5Fe catalysts while higher concentration leads to synthesis of CNF support as observed in 5Fe catalysts.
- Fe active sites undergo reaction with the undercoordinated carbon and carbon generated from coke / char to form Fe₃C / Fe₃C_x.
- Saturation of Fe active sites with undercoordinated in support defects and free-carbon from reaction causes regeneration of the initial GNS / CNF support.
- Two types of in-situ regeneration phenomena were observed in the Fe-Mo₂C catalysts: Type A regeneration involved formation of 3D CNFs over initial graphene nanosheets support in 0.5Fe and 2.5Fe catalysts. Type B regeneration involved formation of graphene cover over underlying CNF support in 5Fe catalysts.
- Fe-Mo₂C catalyst stability was excellent over 15 reforming cycles as evident from TGA oxidation studies and improved particle size distribution in the spent catalysts. Thus, Fe-Mo₂C-

CNF catalyst can be used extensively without external regeneration or replenishment in the modular shale gas assisted biomass reforming reactors.

This research provides fundamental insights in design of a stable catalyst with unique in-situ support regeneration capacity for sustained activity for shale gas assisted biomass reforming to hydrogen rich syngas with carbon dioxide utilization. Innovation reported in in-situ catalyst regeneration over 15 reforming cycles will eliminate the need for external regeneration and reduce the downtime by minimizing the frequency of catalyst bed replenishment. This unique discovery aids process development of catalytic shale gas – biomass co-processing reactor module in a major way.

Chapter 6: Supporting Projects and Future Perspective in Process Development of Modular Shale Gas Assisted Biomass Reforming

Process development of modular shale gas assisted biomass reforming approach was followed by adopting a holistic approach which also includes investigating supporting projects such as effect of ethane addition on biomass reforming, lignin reforming (discussed in earlier section), co-gasification of biomass with other feedstocks including coal and waste plastics, and process scale-up to a bubbling fluidized bed reactor for bench to pilot scale demonstration of the novel co-processing approach. Ethane assisted biomass reforming approach was investigated to determine the effect of ethane addition on biomass conversion to syngas.

6.1 Ethane assisted biomass reforming

Ethane constitutes 16.3 mol.% of the Eagle Ford shale composition which was utilized for reforming biomass at 850°C. Methane activity for biomass reforming has been extensively studied in earlier chapters. Catalyst design and catalyst regeneration studies were also performed using C1 (CH_4 / $\text{CH}_4\text{-CO}_2$) as reaction feed. Fe-Mo₂C-GNS/CNF catalyst has shown excellent activity and stability for reforming of lignin and ligno-cellulosic hardwood biomass feedstock. Ethane activation and ethane assisted hydrodeoxygenation / hydrogenolysis reforming of biomass to syngas at high temperature is important to validate the CH_4 assisted biomass reforming concept for a typical shale / natural gas feedstock. Ethane dehydrogenation in the presence of oxygen showed high selectivity towards ethylene at lower temperatures of 700°C and below over MoO₃/Al₂O₃ catalyst with ~100% oxygen conversion.[146] CO and ethylene selectivity was similar at 700°C for oxidative ethane dehydrogenation with ethane conversion reaching up to 75%. Oxidative dehydrogenation of ethane to light olefins has been extensively studied over different heterogeneous catalyst systems.[147–149] Here, ethane dehydrogenation and activation has been aimed for HDO and hydrogenolysis reforming of biomass to syngas. High oxygen content of hardwood biomass can be effectively utilized for dehydrogenation and partial oxidation of ethane feed to CO. This concept has been explored here to obtain syngas composition from catalytic co-processing with hardwood ligno-cellulosic biomass.

6.1.1 Temperature effect on ethane assisted biomass reforming over Fe-Mo₂C-GNS / CNF catalyst

Figure 70 and Figure 71 shows the syngas composition and H₂:CO ratio obtained from 5 mol.% ethane assisted reforming of hardwood biomass performed at 800°C and 850°C respectively for a time-on-stream of 75 min over 0.5Fe, 2.5Fe, and 5Fe catalysts. As seen in the results, H₂:CO obtained on all three catalysts is less than 2 as compared to methane assisted biomass reforming which produces high H₂ concentration in the syngas. However, excellent HDO conversion has been obtained using ethane (C₂H₆) as the reacting gas feed by replacing methane (CH₄) as seen in Table 20. Compared to HDO conversion from CH₄ assisted biomass reforming over 0.5Fe (48%), ethane addition significantly increases hydrodeoxygenation and hydrogenolysis reforming of biomass. Presence of oxygen on the catalytic surface enhances C₂H₆ activation, dehydrogenation and partial oxidation to CO as reported in several studies. H₂ concentration was highest over 5Fe catalysts as well as the H₂ conversion over 5Fe catalysts (56%). H₂ conv over 5Fe catalyst at 800°C was 14 basis points higher than that on 2.5Fe catalyst and 9 basis points higher than 0.5Fe catalyst. HDO conversion was 20 basis points or higher over 2.5Fe and 0.5Fe catalysts than that obtained on the 5Fe catalyst. Higher Fe concentration catalyst leading to high H₂ conv and lower HDO conversion at 800°C indicates higher thermal catalytic ethane dehydrogenation compared to ethane assisted HDO, hydrogenolysis reforming reactions. However, when the reactions were performed at 850°C, HDO conversion on 5Fe and 0.5Fe catalyst was 90% with similar H₂ and C conversion. HDO conversion obtained from the reactions on 2.5Fe catalyst was much lower compared to the other two catalysts (71%) indicating lower HDO, hydrogenolysis reforming of biomass and higher ethane dehydrogenation. Average H₂ and CO concentration was higher at 850°C as compared to concentration obtained at 800°C. Higher hydrogen and carbon monoxide concentration and molar yield at higher temperature is expected as HDO, hydrogenolysis reforming reactions are highly endothermic. At both 800°C and 850°C, ethylene concentration in the product gas was negligible thus indicating complete oxidation and conversion of C₂H₆ to CO. Table 21 shows gas, coke / char, and liquid tar yield obtained from methane, ethane, and Eagle Ford shale assisted biomass reforming at different temperatures and catalysts. Ethane assisted biomass reforming results in 50 to 60% gas yield, 20 to 35% coke or char yield, and 14 to 22% liquid tar yield. Compared to methane assisted biomass reforming, gas yield is higher and liquid tar yield is lower from ethane-biomass reforming. At 800°C and 850°C, H₂:CO ratio was consistently below 2 which is less than

the H₂:CO ratio desired in the syngas composition. Ideal syngas composition for downstream chemical synthesis would require H₂:CO ratio greater than 2 and less than 3. Next section compares methane, ethane, and Eagle Ford shale assisted biomass reforming syngas composition.

Figure 70 Syngas composition comparison of ethane assisted biomass reforming over 0.5Fe, 2.5Fe, and 5Fe catalysts at temp of 800°C

Figure 71 Syngas composition comparison of ethane assisted biomass reforming over 0.5Fe, 2.5Fe, and 5Fe catalysts at temp of 850°C

6.1.2 Comparison of syngas composition and conversion obtained from CH₄, C₂H₆, Eagle Ford shale assisted biomass reforming

Figure 72 shows comparative syngas composition obtained from methane, ethane, and shale assisted biomass reforming performed at 850°C over 5Fe catalysts. H₂:CO ratio obtained from Eagle Ford shale composition is greater than 2. H₂:CO from CH₄ assisted biomass reforming was highest among the three (3.22) and lowest on ethane assisted biomass reforming (1.65). Eagle Ford shale composition data is provided in Table 5. Reaction conditions for methane, ethane, and Eagle Ford shale assisted biomass reforming is provided in Table 2. CH₄ assisted biomass reforming reaction generates over 60% hydrogen in the syngas with low CO, CO₂ conversion of biomass oxygenates. Thus, HDO conversion is significantly lower in CH₄ – biomass reaction system (48%) than C₂H₆ and Eagle Ford-biomass reaction system – 90% and 100% respectively. Complete

conversion of biomass oxygenates to CO, CO₂ was observed in the shale-biomass reaction system with CO₂ concentration higher than CO concentration in the syngas. Time-on-stream shale assisted biomass reforming using Eagle Ford basin composition performed at 850°C over 5% Fe-4% Mo₂C-CNF catalyst (5Fe) for 45 minutes TOS is shown in Figure 73. Time-on-stream performance of biomass reforming achieved using shale gas shows steady drop in HDO, hydrogenolysis conversion and declining biomass reforming as CO concentration decreases steadily from 25 mol.% to 10 mol.%. H₂, CO₂, CH₄ concentration remain stable for 45 minutes as CH₄ – C₂H₆ balances H₂, CO₂, and CH₄ in the product gas. Variation in CO concentration is the best indicator for HDO and hydrogenolysis biomass reforming achieved through synergistic blending with CH₄, C₂H₆ in the ratio obtained from Eagle Ford basin. Figure 72a) data shows that addition of ethane to methane assisted biomass reforming reaction system in the composition of shale gas increases the H₂:CO ratio while also resulting in complete conversion of biomass oxygenates to CO, CO₂ (100% HDO conv - Table 20). Figure 72b) shows the normalized concentrations of carbon monoxide, methane, and carbon dioxide for the three gas feeds. Methane concentration in syngas decreases with addition of ethane. Table 21 shows that gas yield from shale-biomass reaction system was on the higher side compared to gas yield from other experimental tests – 59.2%. Solid residue in the form of coke / char was also lower for the shale-biomass reaction system – 22% compared to other methane-biomass and ethane-biomass reaction system.

6.1.3 Conclusions

Ethane assisted biomass reforming experiments performed at temperatures 800°C, 850°C conclusively showed that co-processing of actual shale gas with biomass does not have any detrimental effects on the merit of this synergistic co-processing approach in terms of syngas composition or HDO conversion. On the other hand, increasing ethane content in the feed gas actually increases the HDO conversion significantly from ~50% to over 90% on the Fe-Mo₂C catalyst supported on graphene nanosheets (GNS) or carbon nanofibers (CNF). With higher Fe loading catalysts 2.5Fe and 5Fe, ethane dehydrogenation reaction dominates over HDO and hydrogenolysis reactions apparent from increases H₂ concentration and lower CO concentration in the resulting syngas. Ethane activation over transition metal active site occurs favorably in the presence of biomass oxygenates as oxidative ethane dehydrogenation reaction is favored at high temperatures. Ethane addition decreases the H:C_{eff} slightly from 4 to 3 which results in lower H₂ concentration in the syngas compared to CH₄ assisted biomass reforming. However, addition of

actual shale composition ($\text{CH}_4 + \text{C}_2\text{H}_6$) balances the $\text{H}_2:\text{CO}$ ratio in the syngas to ~ 2 which is advantageous for downstream chemical synthesis.

Figure 72 Syngas composition for methane, ethane, and Eagle Ford shale co-processing with biomass for synergistic reforming at temp: 850°C

Figure 73 Eagle Ford shale assisted biomass reforming at 850°C for 45 minutes time-on-stream over 5%Fe-4%Mo₂C-CNF catalyst

Table 20 Methane, ethane, and Eagle Ford shale assisted biomass reforming over 0.5Fe, 2.5, and 5Fe catalysts: HDO, H₂, C conv.

Experiment	Catalyst	HDO Conv (%)	H₂ Conv (%)	C Conv (%)
5% CH₄ at 800°C for 75 min	0.5Fe	48.4	81.6	28.4
5% C₂H₆ at 800°C for 75 min	5Fe	76.3	56.4	41.7
	2.5Fe	98	41.4	52
	0.5Fe	95.4	47.2	48
5% C₂H₆ at 850°C for 75 min	5Fe	90.2	45.3	44.2
	2.5Fe	71	54	38.3
	0.5Fe	91	43.8	45
Eagle Ford shale at 800°C for 45 min	0.5Fe	100	44	39.8

Table 21 Methane, ethane, and Eagle Ford shale assisted biomass reforming-gas, coke/char, and liquid tar yield

Experiment	Catalyst	Gas yield (%)	Coke/char (%)	Liquid tar (%)
5% CH₄ at 800°C for 75 min	0.5Fe	45.7	26.7	27.6
5% C₂H₆ at 80°C for 75 min	5Fe	53	30.4	16.6
	2.5Fe	60.2	20.7	19
	0.5Fe	58.3	23	18.7
5% C₂H₆ at 850°C for 75 min	5Fe	56	27.4	22
	2.5Fe	50.8	34	15
	0.5Fe	56.5	29.6	14
Eagle Ford shale at 800°C for 45 min	0.5Fe	59.2	22.2	18.7

6.2 Process scale-up to bubbling fluidized Bed gasifier (BFBG): preliminary analysis

6.2.1 High temperature fluidized bed hydrodynamics

Fluidization hydrodynamics was investigated in detail in the cold flow test rig by Sivri et al through collaboration with Mechanical and Aerospace Engineering department at West Virginia University.[150] Sand as fluidization bed material along with biomass, coal, and ash was used in binary mixtures in premixed and unmixed before fluidization. Minimum fluidization behavior, spatial variations in pressure along the fluidized bed height, bed pressure drop, minimum fluidization velocity were among the major parameters studied. Fluidizing gas flow (Air / nitrogen) was varied from 0 to 14 SLM. Particle entrainment in the disengagement zone with extensive slugging occurred at higher flow rates (>14 SLM). Cold flow test rig hydrodynamics results in dimensionally identical Acrylic system has been illustrated in detail by Sivri et al.[150] With cold flow baseline analysis, high temperature hydrodynamics was performed in the Inconel gasifier reactor with ID of 1.5 inch. Non-reactive hydrodynamics investigation was performed using 300g of fine sand as bed material with mean particle diameter of 300 microns. Figure 74 shows bed pressure drop (ΔP) measured in KPa against volumetric flow rate of industrial grade nitrogen from 0 to 14 Standard Liters per Minute (SLM). Bed pressure drop increases with increasing gas flow rate as is the case with fluidized bed reactors. Bed pressure drop increases linearly at different rates (different slope) at 200°C, 400°C, 600°C, and 800°C. When the minimum fluidized bed condition is achieved which is indicated by plateauing of bed pressure drop with continuous increase in flow rate. Here, minimum fluidization flowrate is defined from a purely instrumental and operational perspective as the analysis provided here is preliminary. This minimum fluidization flowrate is defined as the superficial gas flowrate at the inlet of the reactor. Detailed analysis of intrinsic gas velocity and its effects on the reactive mass transfer between gas-solid phases of biomass / coal gasification as well the effects on fluidization hydrodynamics can be performed with the preliminary analysis as reference. At this condition, the drag force exerted by the fluidizing gas is equal to the weight (gravitational force) of the bed material. In physical terms, every individual solid particle is separated with the fluidizing gas from each other (uniform homogeneous fluidization). At minimum fluidization state, bed height is generally identical to the static bed height (fixed bed with no gas flow).[151]

Figure 74 High temperature fluidization hydrodynamics in the 1.5 inch bubbling fluidized bed with fluidization data generated at 200, 400, 600, 800°C

Interesting take-away from the high temperature fluidization hydrodynamics investigation was the decrease in minimum fluidization flowrate with increase in temperature. Minimum fluidization flowrate was ~3.75 SLM at 200°C and decreased to ~1 SLM at 600°C and 800°C. Minimum fluidization flowrate decreases by 53% between 200°C to 600°C and by 27% between 200°C to 400°C. However, between 600°C to 800°C, fluidization behavior did not change significantly based on this study. Bed pressure drop at 600°C followed similar behavior to that at 800°C for every incremental change in flow rate. Intuitively, change in pressure drop with temperature is mainly due to thermal expansion and density decrease in fluidizing gas. Behavior between 600°C to 800°C could be similar due to real gas behavior (deviation from ideal gas law) in nitrogen. This real gas behavior could be the reason why nitrogen did not expand significantly at high temperature beyond 600°C thus having similar density at 600°C and 800°C. Moreover, larger variations in bed pressure drop were observed at 600°C and 800°C with incremental increase in fluidizing gas flow rate. At 200°C and 400°C, bed pressure drop was nearly constant (2 to 2.5 KPa) in fluidization and fast fluidization regime. Flow rate of 8 SLM was chosen for reactive chemistry studies on preliminary biomass and coal gasification studies. At 8 SLM, fluidizing gas flowrate is > 2 times of the minimum fluidization flowrate. Uniform fluidization was observed at 8 SLM for 300 g bed

material. Bed pressure drop was between 2.7 to 3.4 KPa at 800°C between 1 to 9 SLM and decreased gradually beyond 9 SLM. Decrease in bed pressure drop between 9 to 14 SLM at 800°C could be the onset of slugging and particle entrainment to the disengagement zone. Thus 8 SLM could be considered as fast fluidization regime for the specific case.[151]

6.2.2 Preliminary hardwood biomass and bituminous coal gasification

Preliminary biomass non-oxidative gasification was performed at temperatures ranging from 800°C to 950°C. Figure 75 shows the typical composition of the product gas from biomass and coal gasification experiments. As seen in the elemental composition of coal, oxygen content is too low (see Table 5) thus requiring an external gasifying agent to produce the desired syngas composition. With the addition of 10 mole% steam to the coal feed, a H₂:CO ratio on average of 3.23 was observed. Syngas obtained from coal is of higher calorific value and quality than that from biomass gasification. Figure 75 compares average yield and H₂:CO of biomass gasification in fixed bed, bubbling fluidized bed (BFB), and coal – 10% steam gasification in BFBG. H₂:CO for non-oxidative biomass gasification in fixed bed is 0.35 which improves by nearly 3 times when the same feedstock is reacted in BFBG. BFBG is operated in the fast fluidization regime which improves reaction kinetics. Nitrogen was used as the fluidization gas for non-oxidative biomass gasification and nitrogen – steam mixture for coal gasification. Feeding started when the reactor wall temperature and reactor bed temperature reached steady state conditions. Steady state temperature is the maximum temperature of the bed and wall achieved for the furnace set points the biomass / coal mixture was fed to the BFBG using a ½ inch OD feeding tube welded on the BFB reactor top flange. Same size tube is welded at the bottom of the flange to carry the feedstock to the fluidized bed. Feeding rate for biomass was 2g per test. Pittsburgh 8 and Kentucky seam coal (which has higher bulk density compared to biomass) is relatively easier to feed. However, the residence time for coal gasification is generally higher than that for biomass. Therefore, coal feeding rate was also limited to 2g for every test. Fluidizing gas flow rate was maintained to 8 SLM. It is known from literature that rapid mixing and uniform fluidization achieves higher contact of gas phase and solid phase molecules in a gas-solid multiphase system [7, 22, 24]. This was also evident from the significant improvement observed in H₂:CO ratio obtained from biomass gasification from BFBG (0.91) compared to fixed bed gasifier (0.35). Since there is theoretically no mixing in fixed bed downdraft gasifier, it acts as a non-ideal plug flow reactor. With uniform fast fluidization, BFBG could act as a non-ideal Continuously Stirred Tank Reactor (CSTR).

Reaction kinetics is [21] also proportional to the frequency and bubble rise velocity as most of the gasification reactions occur in the bubble cloud and wake. Thus, development of high efficiency gasification in the bubbling fluidized bed requires detailed study of fluidization hydrodynamics as well as reaction engineering of the feedstock gasification.

Syngas obtained from the gasification of biomass in fixed bed reactor contained higher CO in comparison to H₂ with H₂:CO ratio of 0.35 compared to the BFBG gasification of biomass which showed syngas composition similar to what is typically observed from gasifying biomass, with H₂:CO ratio of 0.91 (Figure 75). Hardwood biomass used for gasification contains 45 wt.% carbon, 4.65 wt.% hydrogen, and 49.2 wt.% oxygen. If all the hydrogen and carbon from solid biomass are converted to H₂, CO (syngas products), theoretical H₂:CO ratio calculated on molar basis is 0.76. However, some of the carbon is also converted to CO₂, CH₄ due to reactions shown in eq(11, 12, 13, 14, and 15). Therefore, H₂, CO ratio is typically between 1 and 2. Typical bio-syngas composition is as follows: CO 30 to 60 mol.%, H₂ 25 to 30 mol.%, CH₄ 0 to 5 mol.%, and CO₂ 5 to 15 mol.%. Syngas composition obtained from BFBG reactor is very similar to the typically obtained composition from biomass gasification. H₂:CO ratio obtained from BFBG reactor shows better conversion to H₂, CO and low CH₄, CO₂ products. Due to very low oxygen content of bituminous Pittsburgh #8 coal, external gasifying agent 10 mol.% steam was used.

6.2.3 Similarity in biomass gasification and CH₄ – assisted reforming

Preliminary hardwood biomass gasification tests performed on the bubbling fluidized bed gasifier and fixed bed reactor are similar in terms of reaction chemistry and engineering to the flare gas (CH₄) assisted HDO reforming of hardwood biomass. Eq(29-33) show major overall gasification reactions. Methane assisted reforming reactions are quite similar in nature to the typical gasification reactions. Although most of elementary reactions in catalytic CH₄ assisted biomass reforming occur on the Fe / Ni (TM) added Mo₂C active sites, gas phase reaction also occur extensively. Gas phase reactions occur especially in small penultimate product species that are easily desorbed from the catalyst active sites.

Major reactions producing syngas in gasification process are written below:

Water gas shift reaction

Steam methane reforming reaction

Boudard reaction

Methanation reaction

Water gas reaction

With strong baseline of preliminary hardwood biomass gasification tests performed on the BFBG reactor, CH₄ – assisted biomass reforming scale-up will be performed soon on the BFBG reactor.

Figure 75 Hardwood biomass gasification in fixed bed and BFBG reactor without external gasifying agent and coal gasification in the BFBG with 10% steam as gasifying agent at 900°C. Fluidization gas flow rate (nitrogen and nitrogen – steam for coal) was around 8 SLM

6.2.4 Conclusions

A preliminary two-fold investigation was performed for process scale-up of flare gas assisted biomass reforming from lab scale fixed bed to bench to sub-pilot scale bubbling fluidized bed gasifier reactor. The two-fold investigation involved high-temperature non-reactive fluidization hydrodynamics studies as well as preliminary biomass and coal gasification studies to understand the reactive chemistry. High-temperature fluidization hydrodynamics on the BFBG without feedstock also provides key information on effect of temperature on fluidization. Distributor plate pressure drop increases significantly at higher gas velocities at high temperature compared to ambient conditions. As discussed earlier, minimum fluidization flowrate decreased with increase in temperature. Bed pressure drop does not remain constant at high temperature and decreases

overall due particle entrainment out of the fluidized bed. Fast fluidization can be achieved at lower gas flow rates at high temperature. Bed material must have a critical mass to withstand the high forces exerted by rapid gas expansion in the fluidized bed. With 300g of bed material, good fluidization was achieved up to 800°C. For biomass gasification, H₂:CO ratio obtained in the syngas from BFBG was much higher compared to that in downdraft fixed bed gasifier (0.91 versus 0.35). Fluidized bed reactor is more efficient than a fixed bed reactor due to rapid and uniform mixing. Flare gas assisted reforming reactions can be potentially performed with higher efficiency in the BFB reactor compared to lab scale fixed bed setup.

6.3 Preliminary results on co-gasification of biomass, coal, and waste plastics

6.3.1 Reaction conditions:

Non-oxidative catalytic and non-catalytic gasification reactions were performed using a lab scale tubular fixed bed reactor. Reactions were performed at a temperature of 800°C (1073K) for a time-on-stream of 45 minutes. Reactions were performed in semi-continuous mode with downdraft configuration. Oxidative gasifying agent such as steam or air was not used for the gasification reactions. Southern pine biomass comprised of higher content of oxygen comparable to carbon in the form of ligno-cellulosic oxygenates. Adding external gasifying agent would undermine the hydrogen concentration in the syngas with much higher concentration of carbon monoxide and carbon dioxide. Initially, reactions were performed for mixture of biomass and coal in the ratio of 1:3, 1:1, 3:1 to determine the optimum ratio of biomass and coal with higher syngas yield and lower CO₂ concentration. Feedstock was initially dried at 100°C overnight before being subjected to the reforming reactions. After selecting the optimum ratio of biomass and coal mix, a mixture of plastics containing was added. Details of the plastics mixture is shown in Table 22. 50% biomass was used with 3 variations in coal to plastics ratio. Coal to plastics ratio used for the reactions was 3:1, 1:1, 1:3. Overall ratio of biomass:coal:plastics was 50:37.5:12.5, 50:25:25, and 50:12.5:37.5.

The temperature of the tubular reactor bed was raised from ambient temperature to 800°C at heating rate of 10°C min⁻¹. The temperature of the reactor bed was maintained at 800°C for 1 hr. Solid feedstock conversion to gas, liquid, char reached completion in ~45 minutes. Syngas composition was analyzed using a Inficon Fusion micro-GC. Liquid tar compounds were captured using methanol solvent trap dipped in an ice-bath. Methanol was volatilized at 67°C and the liquid

tar compounds were quantified. Overall carbon balance of the gasification reactions performed on the feedstock mixtures is shown in Table 23.

Table 22 Plastics mixture added to co-gasification mix of biomass-coal

Plastics component	Percentage (%)
Polyethylene Terephthalate (PET)	40
High density Polyethylene (HDPE)	18
Polyvinyl chloride (PVC)	5.9
High density Polyethylene (LDPE)	18
Polypropylene (PP)	2
Polystyrene	12
Other (Nylon / acrylic / polycarbonate)	4.1

6.3.2 Gasification of Southern pine biomass and Illinois #6 coal mixture

Figure 76 shows the comparison of average product gas composition obtained from the gasification of biomass and coal mixtures at 800°C. 50:50 (1:1) biomass coal mixture showed highest syngas concentration of 86% with just 14% nitrogen (carrier gas) in the product gas. Moreover, CH₄ and CO₂ was lower for the 1:1 biomass-coal mixture compared to other biomass-coal mixtures. High H₂ and CO concentrations (~33%, 15%) was obtained from the gasification of 50B:50C mix. Higher H₂, CO concentrations indicate better hydrodeoxygenation, hydrogenolysis reactions and conversion of cleaved oxygen to CO, CO₂ syngas components. Meanwhile, H₂:CO ratio obtained from the gasification of this mixture was 2.2 compared to 1.79 and 1.97 from 75B:25C and 25B:75C mixtures. Comparable syngas yield was also obtained from the mixture containing 75% biomass and 25% coal. However, higher CH₄ and CO₂ concentration obtained from the gasification of this mix indicates poor reforming conversion to the desired products – H₂, CO. Syngas concentration in the product gas was lowest on the 25B:75C mixture – 73%. H₂, CO concentration was lowest in the syngas obtained from this mix indicating poor conversion, Higher CH₄ concentration from gasification indicated lower degree of reforming and higher degree of thermal cracking owing to higher temperatures. 50% biomass, 50% coal mix (50B:50C) was considered optimum for co-gasification using plastics blend. Table 23 shows the overall carbon balance in the form of gas yield, liquid tar, and solids residue along with proportion of unaccounted carbon.

Overall carbon balance was performed on dry weight basis of the feedstock mixture. Gas yield obtained from biomass-coal mixture was between 27 to 35 wt.% whereas solids residue between 35 to 60 wt.%.

Gasification results obtained for biomass-coal mixtures indicate that increasing the biomass content of the feed mixture increases the syngas yield and yield of liquid heavy hydrocarbons, poly-aromatic hydrocarbons, and phenolics. Solids residue decreases significantly from 1.2 g (60%) to 0.72 g (36%) when biomass composition was increases from 25 wt.% to 75 wt.%. However, 50%-50% biomass-coal feed mixture when gasified at 800°C showed lowest CO₂, CH₄ concentration and high H₂, CO concentration in the syngas. Thus, 50% biomass and 50% coal composition was selected for gasification studies using waste plastics.

Figure 76 Gasification of southern pine biomass and Illinois #6 coal mixtures: 75% biomass with 25% coal (75B:25C), 50% biomass with 50% coal (50B:50C), 25% biomass with 75% coal (25B:75C) performed at 800°C with total feed amount of 2 g

6.3.3 Gasification of Biomass – coal – waste plastics feed

Feed mixtures was selected based on the results obtained in the previous section. 50% biomass was mixed with a blend of coal and waste plastics in the following ratio: 75% coal – 25% plastics (50B-37.5C-12.5P), 50% coal – 50% plastics (50B-25C-25P), and 25% coal – 75% plastics (50B-12.5C-37.5P). Comparative results for syngas composition obtained from gasification of these mixtures at 800°C is shown below in Figure 77. H₂ and CO concentration is similar from gasification of feed mixtures 50B-37.5C-12.5P and 50B-12.5C-37.5P. High CH₄, CO₂ concentration obtained from the gasification of 50B-25C-25P feed indicates lower HDO, hydrogenolysis reforming reactions and low conversion of CH₄ and CO₂. In contrast feed mixtures using 50B-37.5C-12.5P and 50B-12.5C-37.5P had similar syngas composition and syngas

concentration of 76% and 72%. However, looking at the overall carbon balance shown in Table 23, 50B-12.5C-37.5P feed mixtures is clearly the optimum gasification mix. Increasing the plastics:coal ratio significantly increases the gas yield from 35% to 53% and the solids residue decreases from 50% to 34%. This is consistent with the overall carbon balance observed in the biomass-coal feed mixtures. High coal content in the feed leads to significantly higher solids residue in the form of char and low conversion to syngas. Interestingly, it can be observed from Table 23 that yield of liquid heavy aromatic compounds remain largely unchanged with variation in coal and plastics composition. Liquid tar yield is only affected by the biomass composition in the feed as observed in the carbon balance of biomass-coal gasification. $H_2:CO$ ratio obtained from the gasification of 50B-12.5C-37.5P is 2.34 compared to 2.77 obtained from the gasification of 50B-37.5C-12.5P mix. From Table 23, overall carbon balance shows that addition of plastics to the biomass-coal mix leads to increase in the gas yield as the amount of plastics increases. The results also indicate that gasification conversion of coal to syngas is poor without the addition of external gasifying agent such as steam. Syngas composition data for non-catalytic and catalytic co-gasification of biomass-coal and biomass-coal-plastics is provided in Table 24.

Comparative syngas composition and overall carbon balance from gasification of biomass-coal-waste plastics shown in Figure 77 and Table 23 clearly indicate that optimum gasification feed mixture should have following composition: biomass > plastics > coal. Following feed mixture was thus selected for catalytic gasification studies: 50% biomass – 12.5% coal – 37.5 plastics. Following section compares the results obtained from catalytic gasification using three catalysts: 0.5% Fe – 4% Mo_2C on graphene nanosheets (GNS) support, 5% Fe – 4% Mo_2C on carbon nanofiber (CNF support), and coal liquifaction catalyst – Iron oxyhydroxide sulfate $FeOOH-SO_4$.

Figure 77 Gasification of southern pine biomass, Illinois #6 coal, and waste plastics mixtures: 50% biomass common in all three mixtures. Coal:Plastics ratio of 3:1, 1:1, 1:3. Overall composition: 50B:37.5C:12.5P, 50B:25C:25P, 50B:12.5C:37.5P performed at 800°C

Table 23 Overall carbon balance calculated for gasification of biomass-coal, biomass-coal-plastics mixture and catalytic gasification of biomass-coal-plastics feed.

Feed composition mixture wt.% dry basis		Gas yield Amount (g) wt.% dry basis	Liquid tar yield Amount (g) wt.% dry basis	Solid residue (coke / char) Amount (g) wt.% dry basis	Unaccounted carbon Amount (g) wt.% dry basis
25% biomass - 75% coal		0.55 27.5	0.2 10	1.2 60	0.05 2.5
50% biomass - 50% coal		0.56 28	0.47 23.5	0.87 43.5	0.1 5
75% biomass - 25% coal		0.7 35	0.45 22.5	0.72 36	0.13 6.5
50% biomass - 37.5% coal & 12.5% plastics		0.71 35.6	0.22 11.1	1 50	0.07 3.3
50% biomass - 25% coal & 25% plastics		0.92 46	0.21 10.6	0.8 40	0.07 3.5
50% biomass - 12.5% coal & 37.5% plastics		1.06 53.2	0.22 10.8	0.68 34	0.04 2
Catalytic biomass-coal-plastics gasification					
50% biomass 12.5% coal 37.5% plastics (75% plastics with 25% coal)	0.5% Fe - 4% Mo₂C-GNS	1.25 62.5	0.21 10.5	0.48 24	0.06 3
	5% Fe - 4% Mo₂C-CNF	1.37 68.5	0.20 10.2	0.38 19	0.05 2.3
	FeOOH-SO₄	1.5	0.35	0.12	0.03
		75	17.5	6	1.5

Table 24 Average syngas composition, syngas concentration in the product gas, H₂:CO, and CO:CO₂ ratio obtained from gasification of biomass-coal and biomass-coal-plastics

Feed composition mixture wt.% dry basis		H₂ Mol.%	CO Mol.%	CH₄ Mol.%	CO₂ Mol.%	Syngas %	H₂:CO	CO:CO₂
25% biomass 75% coal		13.9	7	31.7	20.6	73.3	~2:1	~1:3
50% biomass 50% coal		32.7	14.8	18.9	19.8	86.3	~2:1	~3:4
75% biomass 25% coal		16.2	9.1	29.8	26.8	82	~7:4	~1:3
50% biomass 37.5% coal 12.5% plastics		22.9	8.3	28.4	16.6	76.2	~11:4	~1:2
50% biomass 25% coal 25% plastics		15.2	6.6	28.2	17.8	67.8	~12:5	~1:3
50% biomass 12.5% coal 37.5% plastics		21.8	9.3	28	13.4	72.5	~12:5	~7:10
Catalytic biomass-coal-plastics gasification								
50% biomass 12.5% coal 37.5% plastics	0.5%Fe 4%Mo₂C- GNS	30.1	9.9	27.8	17.2	85	~3:1	~2:3
	5%Fe - 4%Mo₂C- CNF	26.3	9.3	31	19.7	86.3	~3:1	~1:2
	FeOOH- SO₄	23	8.9	32.7	22.5	87.1	~5:2	~2:5

6.3.4 Catalytic gasification of 50% biomass – 12.5% coal – 37.5% plastics mix

Catalyst synthesis and preparation methods are described in the previous section. Identical reaction conditions (temp: 800°C, 45 minutes TOS) were employed for catalytic gasification of biomass-coal-plastics feed mixture as used in the non-catalytic gasification studies. Figure 78 shows comparative syngas composition and syngas concentration for the optimum feed mix containing 50% biomass (1 g), 12.5% coal (0.25 g), and 37.5% plastics (0.75 g). Amount of catalyst utilized for these reaction studies was 1.5 g in the ratio of 3:4 with the feed mixture. Three catalysts selected for the gasification studies each have unique properties and advantages compared to traditional catalysts. Graphene and carbon nanofiber supported catalysts have shown excellent activity for biomass and in-situ regeneration capability over 15 high temperature CH₄-CO₂ assisted biomass reforming cycles. Thus, the carbon supported nanocluster dispersed catalysts are expected to show similar behavior when employed for biomass-coal-plastics gasification. The two catalysts undergo regeneration due to variation in the composition of Fe active sites to Fe₃C_x and continuous growth of carbon nanofiber-graphene. Catalyst stability and regeneration studies for CH₄-CO₂ assisted biomass reforming have been reported in detail in the recent publication.[133] Similarly, FeOOH-SO₄ catalyst was used earlier for direct coal liquefaction to oils. FeOOH-SO₄ catalyst showed high activity for coal conversion with moderate yield of oils. Moreover, the FeOOH-SO₄ requires simple precipitation followed by calcination using Iron alum or iron ore. The catalyst can be discarded along with ash and solid residue at the bottom of the reactor bed post-reaction with coal. Low cost of synthesis and replenishment of the FeOOH-SO₄ catalyst would allow for economic scale-up of catalytic biomass-coal-plastics gasification. Figure 78 shows the comparative syngas composition and syngas concentration for the catalytic gasification compared with non-catalytic gasification of biomass-coal-plastics mix. Syngas concentration in the product gas increases from 72% to 85-87% with catalytic gasification. Syngas composition did not change significantly after adding the catalyst. However, CH₄ and CO₂ concentration increased slightly with addition of the catalyst.

Figure 79, Figure 80, Figure 81, and Figure 82 show the time-on-stream syngas composition for the non-catalytic and catalytic gasification of the selected biomass-coal-plastics mixture. Time-on-stream (TOS) syngas composition of non-catalytic and catalytic gasification shows interesting trends. Without the catalyst addition, CH₄ is the dominating product in the syngas over the entire reaction time. Catalytic gasification of the biomass-coal-plastics mixture shows high CH₄, CO₂

concentration in the initial phase of the reaction. In the later phase of the reaction, H₂ concentration increases as seen in Figure 80, Figure 81, and Figure 82. H₂:CO ratio is significantly higher for the 0.5Fe and 5Fe catalysts compared to the non-catalytic gasification and FeOOH-SO₄ assisted gasification of biomass-coal-plastics. H₂:CO ratio was 3 and 2.85 for the reactions performed over 0.5Fe and 5Fe catalysts.

Table 24 shows the average syngas composition with H₂ concentration of 30%, 26%, and 23% for reactions performed over 0.5Fe, 5Fe, FeOOH-SO₄. CO concentration was ~9%. Higher CH₄ concentration indicates higher degree of catalytic thermal cracking while high CO₂ concentration is an indication of further reforming in the form of water gas shift reactions. Overall carbon balance presented in Table 23 shows that gas yield increases substantially with addition of the catalyst to the reacting mixture. Gas yield increased to 62% with 0.5Fe catalyst, 69% with 5Fe catalyst, and 75% with the FeOOH-SO₄ catalyst. Tar yield was around ~10% for the non-catalytic gasification as well as 0.5Fe and 5Fe catalysts. Tar yield increased to 17.5% with FeOOH-SO₄ indicating higher liquefaction of the solid feedstock.

Figure 78 Catalytic gasification of southern pine biomass, Illinois #6 coal, and waste plastics mixture (50B-12.5C-37.5P) over 0.5%Fe-4%Mo₂C-GNS, 5%Fe-4%Mo₂C-CNF, and FeOOH-SO₄ catalysts.

Figure 79 Non-catalytic gasification of southern pine biomass, Illinois #6 coal, and waste plastics mixture: 50% biomass, 12.5% coal, 37.5% plastics. Reaction performed at 800°C with feed amount of 2 g.

Figure 80 Catalytic gasification of southern pine biomass, Illinois #6 coal, and waste plastics mixture: 50% biomass, 12.5% coal, 37.5% plastics. Reaction performed at 800°C over 1.5 g of 0.5%Fe-4%Mo₂C-GNS catalysts at temperature 800°C with feed amount of 2 g.

Figure 81 Catalytic gasification of southern pine biomass, Illinois #6 coal, and waste plastics mixture: 50% biomass, 12.5% coal, 37.5% plastics. Reaction performed at 800°C over 1.5 g of 5%Fe-4%Mo₂C-GNS catalysts at temperature 800°C with feed amount of 2 g.

Figure 82 Catalytic gasification of southern pine biomass, Illinois #6 coal, and waste plastics mixture: 50% biomass, 12.5% coal, 37.5% plastics. Reaction performed at 800°C over 1.5 g of FeOOH-SO₄ catalysts at temperature 800°C with feed amount of 2 g.

6.3.5 Conclusions

Biomass-coal-plastics co-gasification is an alternative process for converting waste plastics and biomass in the form of forest residues, switchgrass, and kraft lignin to syngas with addition of smaller proportion of coal. Co-gasification of biomass, coal, and waste plastics have shown promising results both catalytic and non-catalytic reaction systems. Syngas selectivity defined by the molar composition of H₂, CO in syngas was 80 to 86% on the 0.5Fe, 5Fe, and FeOOH-SO₄. Novelty of the catalytic co-gasification approach adopted here is cost-effectiveness of the catalysts used. Both carbon nanofiber (CNF) and sulfate catalysts studied here have minimal synthesis cost as they are obtained from raw materials such as biomass and iron ore which are either free of cost or have significantly lower cost than the starting materials used for zeolite or other expensive metal

supported catalysts. $H_2:CO$ ratio obtained from the co-gasification of biomass-coal-waste plastics was between 2 and 3 with typical gas yield of 60 to 75% for the catalytic gasification. Addition of catalyst to the gasification feed substantially increased the gas yield from less than 50% to above 65%. Solid residue-coke / char yield dropped significantly when catalytic gasification was performed. Biomass-coal-waste-plastics reforming can also be performed by co-processing with shale gas which further add value to the concept of modular reforming on-site at stranded natural gas producing sites.

7. Publications and Presentations

7.1 Publications:

Published as lead author

1. **Hydrogen-Rich Syngas Production through Synergistic Methane-Activated Catalytic Biomass Gasification.** Amoolya Lalsare, Yuxin, Wang, Qingyuan Li, Ali Sivri, Cosmin E Dumitrescu, Jianli Hu. *ACS Sustainable Chemistry & Engineering*. 2019. DOI: <https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.9b02663>
2. **Biomass – Flare gas synergistic co-processing in the presence of carbon dioxide for the controlled production of syngas ($H_2:CO \sim 2 - 2.5$).** Amoolya Lalsare, Ali Sivri, Ryan Egan, Roman J. Vukmanovich, Cosmin E. Dumitrescu, Jianli Hu. *Chemical Engineering Journal*. 2020. DOI: <https://doi.org/10.1016/j.cej.2019.123783>
3. **Self-Regenerable Carbon Nanofiber Supported Fe – Mo_2C Catalyst for CH_4 - CO_2 Activated Biomass Reforming to Hydrogen Rich Syngas.** Amoolya Lalsare, Brian Leonard, Roman J. Vukmanovich, Cosmin E. Dumitrescu, William Rogers, Jianli Hu. *Submitted to Applied Catalysis B: Environmental*. 2020. DOI: <https://doi.org/10.1016/j.apcatb.2020.119537>

Under review as lead author

4. **Graphene Supported Fe / Ni, β - Mo_2C Nanoparticles: Experimental and DFT Integrated Approach to Catalyst Development for Synergistic Hydrogen Production Through Lignin Rich Biomass Reforming & Reduced Shale Gas Flaring.** Amoolya Lalsare, Tuhin S. Khan, Brian Leonard, Roman J. Vukmanovich, Pedram Tavazohi, Lili Li, Jianli Hu. *Accepted at ACS Catalysis*. December 2020

Published as co-author

5. **Microwave Plasma-Enhanced and Microwave Heated Chemical Reactions.** Sarojini Tiwari, Ashley Caiola, Xinwei Bai, Amoolya Lalsare, Jianli Hu. *Plasma Chemistry and Plasma Processing*. 2019. DOI: <https://link.springer.com/article/10.1007/s11090-019-10040-7>

Under review as co-author

6. **Experimental investigation of the temperature effect on the hydrodynamics of a bench-scale bubbling fluidized-bed.** Ali Sivri, Amoolya Lalsare, Cosmin E Dumitrescu, Jianli Hu Manuscript submitted. 2020

7.2 Technical presentations

2020

- Development of Novel Hydrogen Production Processes for the Transition from Fossil to Renewable Energy Sources (Poster), Amoolya D. Lalsare, I-Wen Wang, Lili Li, Robert Dagle, Jianli Hu, International Congress on Catalysis (ICC-NAM), June 2020 (Scheduled), San Diego, TX
- Self-Regenerable Carbon Nanofiber Supported Fe – Mo₂C Catalyst for CH₄-CO₂ Activated Biomass Reforming to Hydrogen Rich Syngas., Amoolya Lalsare, Brian Leonard, Roman J. Vukmanovich, Cosmin E. Dumitrescu, William Rogers, Jianli Hu. November 17 2020. Virtual AIChE National Meeting 2020
- Graphene Supported Fe / Ni, β -Mo₂C Nanoparticles: Experimental and DFT Integrated Approach to Catalyst Development for Synergistic Hydrogen Production Through Lignin Rich Biomass Reforming & Reduced Shale Gas Flaring. Amoolya Lalsare, Tuhin S. Khan, Brian Leonard, Roman J. Vukmanovich, Pedram Tavazohi, Lili Li, Jianli Hu. November 18 2020. Virtual AIChE National Meeting 2020

2019

- Biomass – Flare Gas Synergistic Co-processing to Produce Hydrogen Rich Syngas with CO₂ Utilization, Amoolya D. Lalsare, Tuhin S. Khan, Yuxin Wang, Qingyuan Li, Brian Leonard, Roman Vukmanovich, Jianli Hu, AIChE Fall National Meeting, Nov 2019, Orlando, FL
- Synergistic Natural Gas – Biomass Co-processing to Produce Hydrogen Rich Syngas, Amoolya D. Lalsare, Jianli Hu, Ali C. Sivri, Cosmin E. Dumitrescu, Multi-phase Flow Science Workshop, August 2019, Morgantown, WV
- Shale Gas & Biomass Co-Gasification for Syngas Production, Amoolya D. Lalsare, Jianli Hu, Ali C. Sivri, Cosmin E. Dumitrescu, 12th AIChE Natural Gas Symposium, June 2019, San Antonio, TX

2018

- Catalytic Conversion of Biomass to Value Added Chemicals and Fuels (Poster), Amoolya D. Lalsare, Yuxin Wang, Ali C. Sivri, Basel Rasheed, Cosmin E. Dumitrescu, Jianli Hu, AIChE Fall National Meeting, Nov 2018, Pittsburgh, PA
- Catalytic Conversion of Biomass to Value Added Chemicals and Fuels (Poster), Amoolya D. Lalsare, Yuxin Wang, Ali C. Sivri, Basel Rasheed, Cosmin E. Dumitrescu, Jianli Hu, ACS Fall National Meeting, Aug 2018, Boston, MA
- High Efficiencies Gasification Techniques Development and Parametric Reaction Kinetics Investigation for Biomass and Coal, Amoolya D. Lalsare, Yuxin Wang, Ali C. Sivri, Basel Rasheed, Cosmin E. Dumitrescu, Jianli Hu, NETL Multi-phase Flow Science Workshop, Aug 2018, Houston, TX
- Renewable Energy to Fuels through Microwave Plasma Catalytic Reactor, Amoolya D. Lalsare, Xinwei Bai, Sarojini Tiwari, Ashley Caiola, Jianli Hu, ASEE Symposium, Jan 2018, Washington D.C

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