Chapter: 1

Introduction

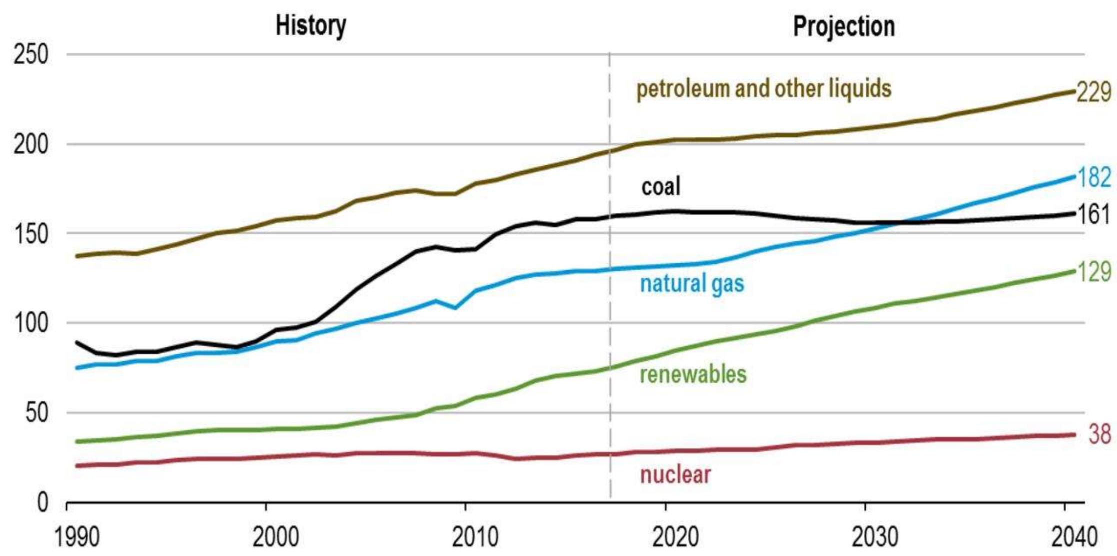
1.1 Introduction

Energy is essential for human survival and socio-economic development. The continuously growing demand for energy in the world represents a matter of concern. In 2016, the worldwide energy consumption per year was equivalent to 13,275 Million tonnes of oil[1, 2]. The economic growth of any country largely depends on its energy infrastructure. Because of the increasing population and urbanization and global industrialization, the world's energy requirement is growing tremendously. However, presently available sources are not enough to fulfill these needs completely. Currently, these energy demands are being fulfilled mainly by fossil fuel reserves like natural gas, coal, petroleum.

Moreover, intensified use of fossil fuels has also increased due to increased energy consumption. Unfortunately, these fossil fuel reserves are non-renewable and depleting rapidly day by day and likely to be worn out within few decades. Goyal et al. reported that inflation of oil prices in the international market is majorly dependent on oil source availability and is expected to be depleted by 2050 [3]. Even in the present time, energy shortage is becoming a worldwide problem. The International Energy outlook 2017 (IEO2017) forecasts that world primary energy consumption between 2015 and 2040 will increase by 28%. Most of this growth is expected to come from developing countries where demand is driven by strong economic growth, particularly in Asia (China and India). **Fig 1.1** shows that higher economic growth drives increasing energy consumption. Besides this high energy consumption, the demand for other energy sources (oil etc.) still depends mainly on imports, which is also continuously increasing over the years. At present, 75 to 80 percent of the world's energy comes from fossil fuel sources [4, 5]. Continuous utilization of fossil fuels leads to their exhaustion [6]. The average amount of lifecycle CO_2

generation during electricity production from coal is about 888 tonnes CO_2 e/GWh, followed by oil and natural gas, about 733 and 499 tonnes CO_2 e/GWh, respectively [7]. Moreover, the consumption of these carbon-based fossil fuels causes severe waste gas emissions, *viz.* sulfur dioxide, nitrogen dioxide, hydrogen chloride, unburn hydrocarbons and carbon monoxide, which causes environmental pollution when its effluent gases are released into the environment [8]. Carbon dioxide (CO_2), which is the combusted product, is a greenhouse gas (GHG) responsible for global warming [9]. It increases the average temperature of the earth, affecting all the ecosystems [10, 11].

World energy consumption by energy sources (quadrillion BTU)



Source: EIA, International Energy Outlook 2018

Fig. 1.1. World energy consumption

The Energy Information Agency (EIA) projected the energy-related carbon dioxide emission increase from 33.2 billion metric tonnes in 2015 to 39.36 billion metric tonnes in 2040 (Fig. 1.2) [12]. As a result of all the above concerns viz increasing energy, depletion of conventional energy sources and adverse effect of its consumption on the global environment have forced to investigate environmentally clean, renewable, sustainable cost-effective and alternative energy sources and its facile production worldwide [13] [14].

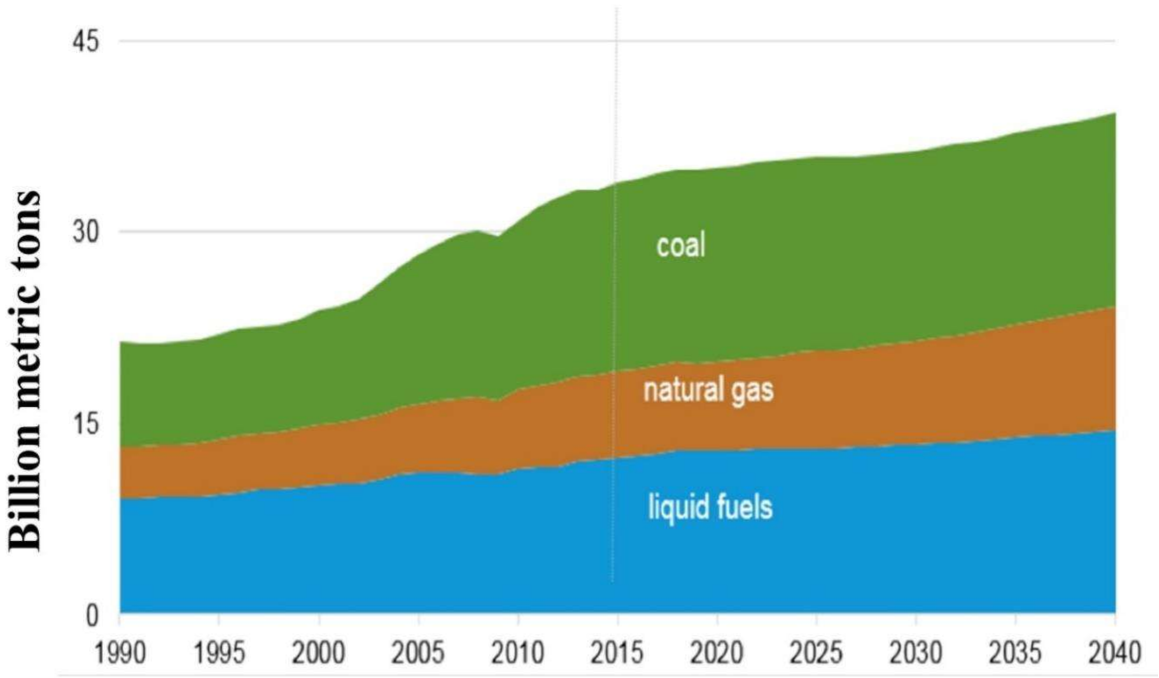


Fig. 1.2. Worldwide projection of carbon dioxide emission[12]

Nowadays, the production of renewable energy through renewable and sustainable technologies is underway on the global level. Fig.1.1 described that there would be a huge demand for energy to meet the need of the world for livelihood, economic development, and socio-development. This immense energy requirement in the future can be achieved by generating energy from renewable energy resources. Particularly, solar, wind, geothermal, hydroelectric and biomass are considered renewable sources. The shift from fossil fuel-based energy to renewable is challenging and overwhelming, but undoubtedly it can be achieved. India can generate energy from utilizing renewable resources because the country has plenty of renewable energy resources.

In current times, because of the depletion of fossil fuel resources and growing concern related to increasing pollution, hydrogen is widely accepted as a promising alternative and sustainable for transportation fuel [15, 16]. It offers several benefits and possesses high energy content (~122 MJ kg^{-1}), which is 2.8 times more than conventional fossil fuels and no generation of any pollutant on combustion as water is the only product formed during the combustion process [17]. Currently, H_2 is mainly generated via steam reforming of natural gas or petroleum-based sources and through coal gasification [18, 19]. However, these sources emit greenhouse gases, contribute to environmental pollution, and lead to the exhaustion of fossil reserves [8, 20]. Alternatively, hydrogen can be produced using renewable energy sources such as biomass either through thermochemical processes such as direct gasification combined with water gas shift reaction or production of bio-oil via fast pyrolysis steam reforming and via biological processes [21] [22-24]. Biomass is the largest sustainable and renewable energy source globally, abundantly among all available resources [25]. Hydrogen production from renewable biomass can mitigate environmental pollution as well as decrease dependency on fossil reserves. Bio-oils or pyrolysis oil obtained through fast pyrolysis of biomass and subsequent catalytic steam reforming has been considered an economical and feasible way to generate hydrogen without harmful greenhouse gas emissions.

Moreover, steam reforming of bio-oil is considered a renewable and sustainable route for hydrogen production due to CO_2 neutral source of biomass growth [26]. Steam reforming of organic compounds is an important procedure for producing hydrogen for on-site use in hydrogenation or fuel cells [27]. Bio-oil, produced from fast pyrolysis of biomass, is highly complex and contains various oxygenated compounds like acids, esters, aldehyde, ketones, sugars, phenols, furfural, as well as many other compounds [23, 28]. Coking is a major challenge in the steam reforming of bio-oil. Considering the complex nature of bio-oil, it is still a key challenge to develop and design an efficient and stable catalyst for hydrogen production from bio-oil steam reforming. Acetic acid (AcOH), one of the main components of raw bio-oil (up to 19 wt.%)[29, 30], has been chosen as a representative compound of bio-oil to explore and develop an efficient catalyst for hydrogen production. AASR takes place via acetic acid decomposition (Eq. (1)), followed by the water gas shift reaction

(WGSR) Eq. (2) simultaneously in the reactor. The overall steam reforming reactions is shown in Eq. (3).

$$CH_3COOH \rightleftharpoons 2CO + 2H_2 \quad (1) \quad \Delta H = +213.4\ kJ/mol$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (2) \quad \Delta H = -41.0\ kJ/mol$$

$$CH_3COOH + 2H_2O \rightleftharpoons 2CO_2 + 4H_2O \quad (3) \quad \Delta H = 131.4\ kJ/mol$$

Acetic acid steam reforming (AASR) also involves complex reaction network pathways, which produces several undesired intermediates causing the generation of carbonaceous species over the catalyst surface. Several researchers investigated various strategies, including modification of catalysts to enhance the production of H_2 and minimization of the intermediate gases during AASR. Catalysts deactivation via coking is a severe issue during the AASR. The most serious problem of coking is clogging the reactor and causing catalyst deactivation [31], which increases the operation cost in the process. Development of the robust catalyst with a high resistivity towards coking has focused on numerous studies on steam reforming of various organics [32]. The coke formation is associated with various side reactions such as cracking, dehydration, and polymerization reaction on the acidic sites of support material. The reforming activity and selectivity of Ni-based catalysts depend on many factors, *viz.* catalyst preparation methods, types of support, metal loading, use of the additive, and operating conditions[33]. With the active metal phase, proper support is also required to improve activity and stability by alleviating coke deposition during AASR.

1.2 Problem Statement

The production of catalysts requires chemical methods, toxic chemicals for their completion, and long reaction times[34]. Moreover, precise control over the chemical composition, morphology, and microbiological properties remains challenging for scientists and engineers to synthesize cost-effective catalytic nano-size catalysts at a bench scale and then process it extensively for industrialization. This is because the physical and chemical properties of nanoparticles are relatively altered from their bulk ingredients. Therefore, current research has been dedicated to enhancing the porosity, morphology and effective costs of crystalline nanomaterials that are to be used as catalysts. In this respect, metal-organic frameworks (MOFs) have shown outstanding potential because of their controllable structure, unique electrochemical properties and large surface areas [35]. The use of MOFs for clean energy production has been widely considered. Several researchers have prepared heterogeneous catalysts via MOFs. These methods have significantly improved the efficiency, stability and reusability of catalysts. However, these methods can produce specific catalysts and cannot produce a wide range of heterometallic catalysts. Therefore, there is a high demand for a suitable method to formulate a wide range of the required heterometallic catalysts for industrial processes. Beside this the process must be environment friendly and cost-effective.

Moreover, the coke deposition during the reforming reaction remains a major challenge. A possible solution for preventing catalyst deactivation could be utilizing effective support materials to neutralize the acidic sites that would otherwise be subject to coking and sintering processes. Support materials also influence the metal support interaction as well as the reaction mechanism[36].

In order to neutralize the acid sites of γ-Al_2O_3 support, addition with basic promoters such as alkali and alkaline metals (Li, K, Mg, Ca, Ba, etc.) are usually reported in works of literature [33, 37-40]. Furthermore, taking into account the problem of deactivation of catalysts due to coke deposition and sintering at the high reaction temperature, the addition of the small amount of rare earth metals such as cerium and lanthanum to the alumina support is reported, which enhances the catalytic performance[8, 41] by altering the electronic distribution and metal dispersion of active metal via taking participation in the reactions [42, 43]. Furthermore, the addition of La_2O_3 improves the thermal resistance of Al_2O_3; it strongly interacts with Ni active phase and increases dispersion of the fine nickel particles over alumina and thus prevents sintering of metallic Ni particles [44, 45].

This work aims to develop a process to synthesize nano-sized porous nickel supported on modified $Al_2O_3/La_2O_3/CeO_2$ (ALC) catalysts with enhanced sustainable and green hydrogen production from bio-oil and its model compounds.