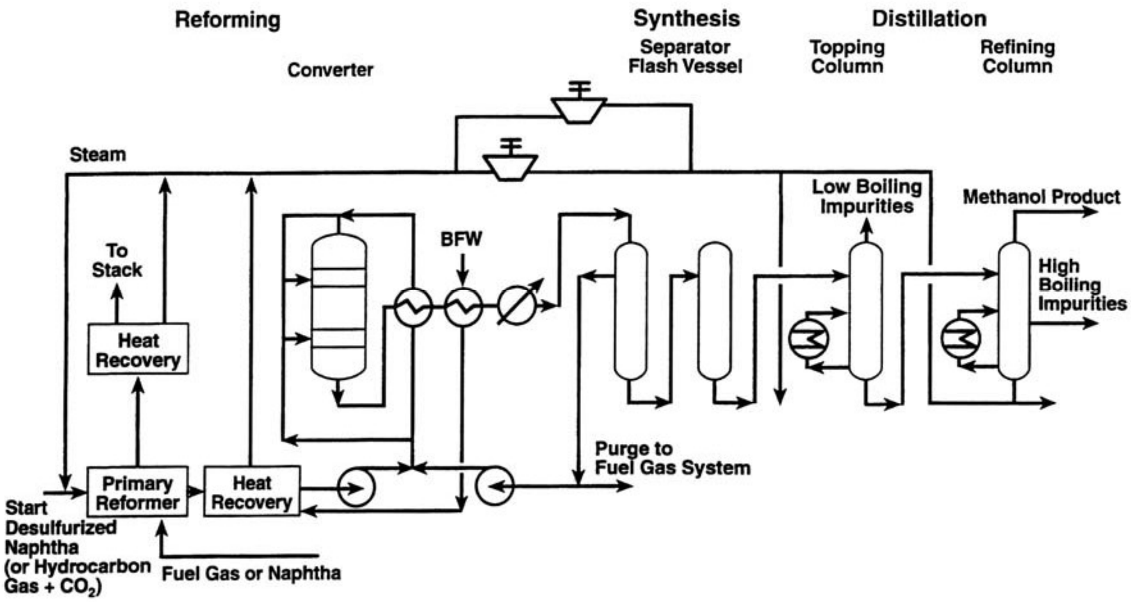

Figure 4.3 - Methanol.[1] (Reprinted with permission from "Refinery Process Handbook," *Hydrocarbon Processing,* Houston, TX: Gulf Publishing, 1968)

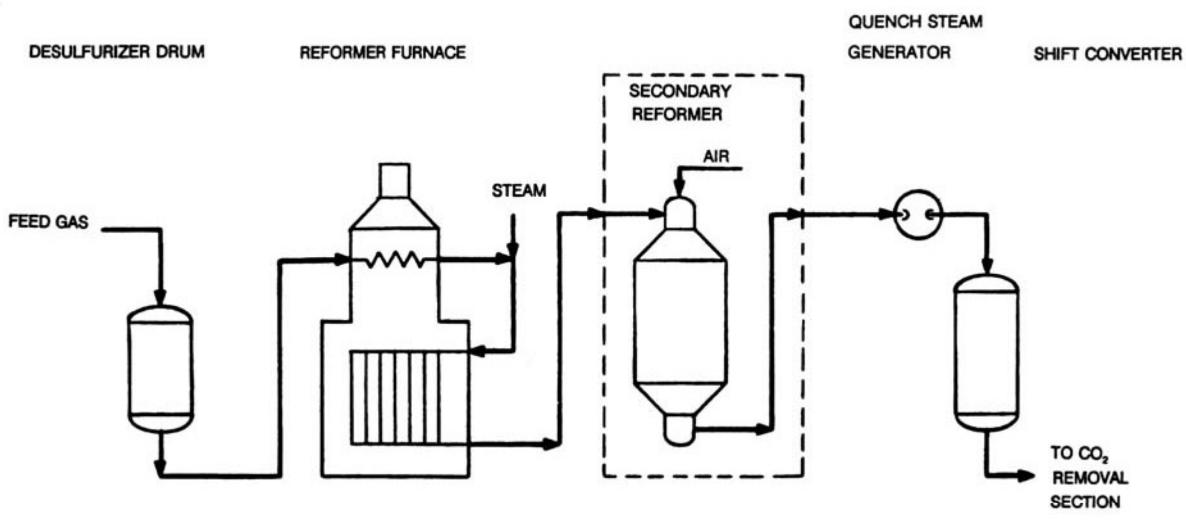

Figure 4.4 - High temperature front end section of reforming plant.[2]

the metal temperature exceeds 425°C to 455°C (800°F to 850°F), 1 Cr-1/2 Mo or 1-1/4 Cr-1/2 Mo is used to avoid long-term deterioration of the mechanical properties by graphitization. Preheat coils in the top of the reformer furnace usually are 2-1/4 Cr - 1 Mo up to 650°C (1,200°F) metal temperature and 304H (UNS S304009) for metal temperatures above 650°C (1,200°F). Caustic stress corrosion cracking from solids can occur in the steam preheat coils if solid carryover is excessive (see Chapter 1, Section 3.7). The inlet connections to the steam methane reformer furnace tubes are either 1-1/4 Cr-1/2 Mo (595°C [1,100°F] maximum) or 2-1/4 Cr-l Mo (650°C [1,200°F] maximum).

The methane (or naphtha) and steam are converted to hydrogen and carbon monoxide along with some carbon dioxide over a nickel catalyst in the HK-40 (UNS J94204) or HP modified, also called CE20N (UNS J92802) primary reformer furnace tubes. CE20N (UNS J92802) has largely replaced HK-40 because of superior stress-to-rupture strength (e.g., 12.55 MPa [1.82 ksi] vs 8.3 MPa [1.2 ksi] at 980°C [1,800°F]). Skin temperatures on these tubes are about 980°C (1,800°F), and the outlet process temperature is about 820°C (1,500°F). Sulfur content in the fuel gas is limited to 2,000 ppm to 3,000 ppm hydrogen sulfide to avoid accelerated oxidation of the outside of the tubes. The tubes are centrifugally cast. They have been used in the as-cast condition which includes about 2.4 mm (3/32 in.) dross and unsoundness on the inside diameter. Currently, most tubes are bored on the inside to remove the dross and unsoundness and machined on the outside. Since the tubes are operating in the range where sigma phase (a brittle Fe-Cr compound) forms, the Cr, Ni, and C are "balanced" to minimize sigma phase embrittlement. The welds must be blasted to remove all residual weld slag; otherwise, the residual weld slag can form a eutectic with the metal oxides, which results in catastrophic oxidation.

The outlets of the primary reformer furnace tubes are connected to either a refractory-lined steel or (occasionally) an alloy 800H (UNS N08810) outlet header with alloy 800H "pigtails." Pigtails are tubes (about 25.4 mm [l in.] in diameter) connected to a reducing cone or a side boss at the bottom of the centrifugally cast tube. They are called pigtails because they were originally made in a double loop configuration to compensate for thermal expansion. More advanced designs have eliminated the need for the loops. Premature failure of alloy 800 (UNS N08800) pigtails has occurred because of too fine a grain size (smaller in size than ASTM No. 5); however, these problems can be avoided by specifying alloy 800H. Some refiners prefer single-row reformer tubes to minimize the thermal stresses on the pigtails.

For temperatures over 650°C (1,200°F), 65 Ni-15Cr-Fe filler metal, such as INCO82™ (UNS N06082) or INCO A™ (UNS W86133), should be used (although INCO A has a somewhat lower creep strength than INCO 82). Neither INCO 92™ (UNS N07092) nor INCO 182™ (UNS W86182) should be used above 480°C to 510°C (900°F to 950°F), because they embrittle when exposed to high temperatures. In addition, INCO 182 has a significantly lower creep strength than either INCO 82 or INCO A. Weld filler metal from other sources should be examined very carefully because some filler metals are subject to "green rot" (preferential oxidation of chromium that occurs about 730°C [1,350°F], resulting in rapid deterioration). For the same reason, alloy 600 (UNS N06600), either wrought or cast, should not be used above 730°C (1,350°F) in this service.

A transfer line connects the primary reformer to the quench steam generator in a hydrogen plant and to the secondary reformer in an ammonia plant. The secondary reformer in an ammonia plant is connected to the quench steam generator by another transfer line. Transfer lines normally operate at 788°C to 980°C (1,450°F to 1,800°F) and usually are made of either alloy 800H (UNS N08810) or refractory-lined carbon steel. Above about 820°C (1,500°F), the combination of low strength and high thermal expansion of metals makes refractory linings attractive; however, refractory linings can develop hot spots from cracks and sometimes can deteriorate due to condensation of corrosive gases at the metal wall.

The secondary reformer in an ammonia plant is a carbon steel vessel with a dual-layer refractory lining. Internal temperatures reach about 1,090°C (2,000°F) from burning as a result of air added through a burner at the top of the vessel to the feed gas (hydrogen, carbon monoxide, carbon dioxide, and steam). The burner is a refractory-lined device subject to failure if not carefully designed. Quench steam generators have refractory-lined inlet channels and tube sheets. Tubes often are made of carbon steel because the heat transfer from the steam on the outside of the tube is markedly better than that from the synthesis gas inside the tube. As a result, the metal temperature closely approaches that of the steam. The inlet ends of the tubes are protected from the inlet gas by ferrules, usually 310 SS (UNS S31000) with insulation between the ferrule and the tube. The tube material should be selected according to the maximum anticipated metal temperature and to API 941. The outlet channels usually are made of low-alloy steel selected by using API 941.

2.2 Carbon Dioxide and Hydrogen Sulfide Removal

After the synthesis gas leaves the quench steam generator, it goes through a shift converter to convert more of the synthesis gas to hydrogen and the carbon monoxide to carbon dioxide. Some ammonia is formed in the shift converter when nitrogen is present. Alloy selection is based on API 941 until the synthesis gas is cooled below the dewpoint (usually about 160°C [325°F]). When wet carbon dioxide condenses out of the synthesis gas, severe corrosion of carbon and low alloy steel results, particularly in turbulent areas. Type