TABLE 19.14 Summary of Effects of Process Parameters on Coal Pyrolysis

Heating rate

- A rapid heating rate increases liquid/gas yield and reduces char yield
- A rapid heating rate produces poorer quality (lower H/C ratio) tar than that obtained at a slower heating rate[19,20]
- A rapid heating rate (in a reactive gas atmosphere) produces char with increased open structure and reactivity
- A rapid heating rate increases the thermoplastic (softening and swelling) behavior of coal
- Achieving a rapid heating rate requires a sophisticated (often expensive) system

Temperature

- Low-temperature operation (500–700°C) improves liquid yield
- Temperature affects heteroatom distribution among char, liquid, and gas
- At elevated temperatures (>1300°C), inorganics are removed as slag
- Lower temperatures require a longer residence time for complete reaction

Pressure

Inert gas atmosphere:

- Higher pressure operation reduces reactor size (i.e. increases throughput)
- Higher pressure reduces tar yield
- Coal feeding and product separation are more difficult at high pressure
- Higher pressure improves gas–solid heat transfer

H_2 atmosphere:

- Improves the yields of liquid and lighter products
- Requires a sophisticated pressure control system
- May increase undesirable agglomerating properties of coal[34]
- H_2 cost must be compared to the increased value of the product

Other atmospheres (H_2O, CO_2, CO, CH_4, CS_2):

- Probably improve liquid–gas yield
- Little information available

Vacuum:

- Plastic behavior of coal is reduced[23]
- Increases liquid/gas yield[23]
- Difficult to achieve gas–solid heat transfer (solid–solid heat transfer feasible)
- Little information available

Particle size

- Smaller particle size improves gas–liquid yield
- Smaller particle size reduces secondary reactions
- Grinding cost increases with the reduction in size

Coal rank

- High Volatile A (HVA) bituminous coals produce the largest quantity of tar
- Lignites are rich in oxygen functional groups that lead to overall reduction in the calorific value of the product
- The type of sulfur (pyritic versus organic) present influences sulfur distribution among the products

Many excellent reviews (Howard,[32] Gavalas,[3] and Solomon and Serio[33]) have been published that discuss the factors affecting coal pyrolysis and product composition. In the following sections, major conclusions presented in the literature are discussed (as summarized in Table 19.14).

Temperature and Heating Rate. Coal undergoes many physical and chemical changes when heated gradually from ambient temperature to approximately 1000°C. Some changes, such as carbon–carbon bond scission, are observed before the onset of thermal decomposition that occurs above 350°C. When heated to approximately 100°C, physically sorbed moisture is liberated. Heating low-rank coals, such as lignites, that contain appreciable carboxylic functional groups will liberate carbon dioxide by thermal decarboxylation. Over 50 percent of the carboxylic acid functional groups are lost in the temperature range 100–250°C.

As the temperature of thermal treatment increases to the range 200–400°C, coal produces a number of lower molecular weight organic species (especially aliphatic compounds), which are believed to arise from components that are loosely bound to the more thermally stable part of the coal structure. At a higher temperature (375–700°C, depending on the heating rate), thermal destruction of the coal structure occurs, as reflected by the formation of a variety of hydrocarbons, including methane, other alkanes, polycyclic aromatics, phenols, and nitrogen-containing compounds. In this temperature range, bituminous coals soften and become plastic (thermoplastic) to varying degrees.

At still higher temperatures (600–800°C, depending on the heating rate), the plastic mass undergoes repolymerization, forming semicoke (solid coke containing significant volatile matter). At temperatures exceeding 600°C, semicoke hardens to form coke with the evolution of methane, hydrogen, and traces of carbon oxides. Pyrolysis of coal is essentially complete at approximately 1000°C. The temperature at which the maximum devolatilization rate occurs depends on the heating rate. For a slow heating rate (about 5°C/s) the maximum rate occurs at around 400°C, whereas for a rapid heating rate (about 10°C/s) the maximum rate might not occur until 900°C.[35] Maintaining the coal at the final temperature for an extended period normally increases the yield of volatile material, because char decomposition is a relatively slow process.

Because pyrolysis reactions do not occur at sharply defined temperatures, the heating rate has a marked effect on the nature and distribution of pyrolysis products, as summarized in Table 19.14. Solomon and coworkers conducted extensive work on the kinetics of coal devolatilization, and many reviews are available.[36]

Coal Rank. The type of coal strongly influences pyrolysis behavior. Low-rank coals, such as lignite, contain oxygen functional groups that evolve water and carbon oxides upon pyrolysis. Higher-rank bituminous coals contain less oxygen; consequently, these coals produce significantly less water and carbon oxides when pyrolized. The nature of the tar produced is also dependent on coal rank. Bituminous coal tars tend to be more aromatic (and relatively more thermally stable) than the tars generated from lignites. When heated, bituminous coals soften, become plastic, and swell to varying degrees, whereas lower-rank coals generally do not become plastic. However, at a rapid heating rate (about 10°C/min) or elevated pressure, certain lower-rank coals may melt and demonstrate some plastic and swelling characteristics.

Other Factors. Several other factors influence, at least to some extent, the course of the pyrolysis process. These include particle size, bed configuration, pressure/vacuum during pyrolysis, nature of the coal ash, secondary reactions, etc.[37] It is beyond the scope of this chapter to consider these items, but the interested reader can find additional information in the literature, including reports on pressure effects,[21,38] effect of vacuum,[23] effect of inorganics,[26,39] and effect of a reactive atmosphere.[23,40]

Utilization and Characterization of Pyrolysis Products

Efficient utilization of all the products, solid, liquid, and gaseous, is essential if favorable economics for a pyrolysis process are to be achieved. Products may require varying degrees of treatment before they are usable. The stream exiting the pyrolyzer requires separation of gas, liquid, and particulates, similar to the situation for a fixed-bed gasifier (i.e., cold gas cleanup). Possible operations include hot dust removal cyclones, quench/particulate scrubber towers, and venturi scrubbers to remove tar mist. In general, gas stream sulfur removal and wastewater treatment are also required. Finally, environmental factors, such as toxicity,[41] carcinogenicity, and mutagenicity of the coal pyrolysis liquids (CPL), need to be considered. For example, the mutagenicity of CPL is strongly dependent on the conditions of pyrolysis (temperature, coal type, and atmosphere during pyrolysis).

Liquid fuels markets tend to have product specifications that do not vary widely. However, the characteristics of CPL can vary