

## NOMENCLATURE FOR PYROLYSIS EXPERIMENTS INVOLVING H<sub>2</sub>O

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The importance of H<sub>2</sub>O in laboratory pyrolysis experiments designed to simulate natural processes is well documented in studies of coalification (Berl and Schmidt, 1932; Schuhmacher et al., 1960) and petroleum formation (Jurg and Eisma, 1964; Lewan et al., 1979). Industrial pyrolysis processes also benefit from the presence of H<sub>2</sub>O as demonstrated in oil-shale retorting (Gavin, 1922, p. 181), conversion of coal to oil (Fischer, 1925, p. 180), heavy oil upgrading (McCullum and Quick, 1976a and b), and conversion of organic refuse to oil (Appell et al., 1971 and 1975). As experimental work continues to indicate that the phase as well as the presence of H<sub>2</sub>O are important in natural and industrial processes, a nomenclature for pyrolysis experiments involving different H<sub>2</sub>O phases is needed to improve interlaboratory communication and comparison of results. The following nomenclature is proposed to meet this need.

**Hydrous pyrolysis** as originally defined by Lewan and others (1979) denotes experiments in which a sample is pyrolyzed in contact with H<sub>2</sub>O liquid. This condition best represents subsiding sedimentary basins in which the pores and fractures in sedimentary rocks are usually filled with water. As shown in Figure 1, the upper temperature limit for pure H<sub>2</sub>O in this type of pyrolysis is 374°C, but higher temperature limits in excess of 600°C may be obtained by the addition of soluble salts (i.e., NaCl). H<sub>2</sub>O in hydrous pyrolysis experiments typically occurs as both liquid and vapor, unless pressure regulators are employed to maintain only a liquid phase. It is important in the vapor/liquid H<sub>2</sub>O system to optimize the amount of water used for specific reactor and sample volumes to insure that the sample is completely submerged in the liquid phase during pyrolysis (Lewan, 1993).

**Supercritical H<sub>2</sub>O pyrolysis** denotes experiments in which a sample is pyrolyzed in contact with a supercritical fluid containing more than 50 mole % H<sub>2</sub>O. Although the lower temperature limit for pure water in this type of pyrolysis is 374°C, this critical temperature may be lowered below 300°C with the addition of CO<sub>2</sub> to the system (Figure 1). Supercritical H<sub>2</sub>O pyrolysis represents deep crustal regimes where metamorphic grades in excess of greenschist facies occur.

**Steam pyrolysis** is more difficult to define because sedimentary organic matter and its accompanying rock usually generate or liberate minor amounts of H<sub>2</sub>O during experiments commonly referred to as **dry** or **anhydrous pyrolysis**. The headspace in these experiments is typically sufficient for the minor amounts of

evolved H<sub>2</sub>O to occur as vapor at a partial pressure dictated by the available volume and experimental temperature. As an operational definition, it is suggested that steam pyrolysis denotes experiments in which a sample is pyrolyzed in contact with H<sub>2</sub>O vapor at partial pressures in excess of 20 percent of its saturated vapor pressure at experimental temperatures. Steam pyrolysis represents localized near-surface conditions where geothermal vents or subaerial volcanoes are active.

Hydrous, supercritical H<sub>2</sub>O, and steam pyrolysis may be collectively referred to as hydrothermal pyrolysis or aquathermolysis (e.g. Siskin et al., 1990). These collective names are particularly useful for referring to pyrolysis experiments in which insufficient information is given to assess the H<sub>2</sub>O phases present or the phase in which a reaction has occurred at experimental conditions.

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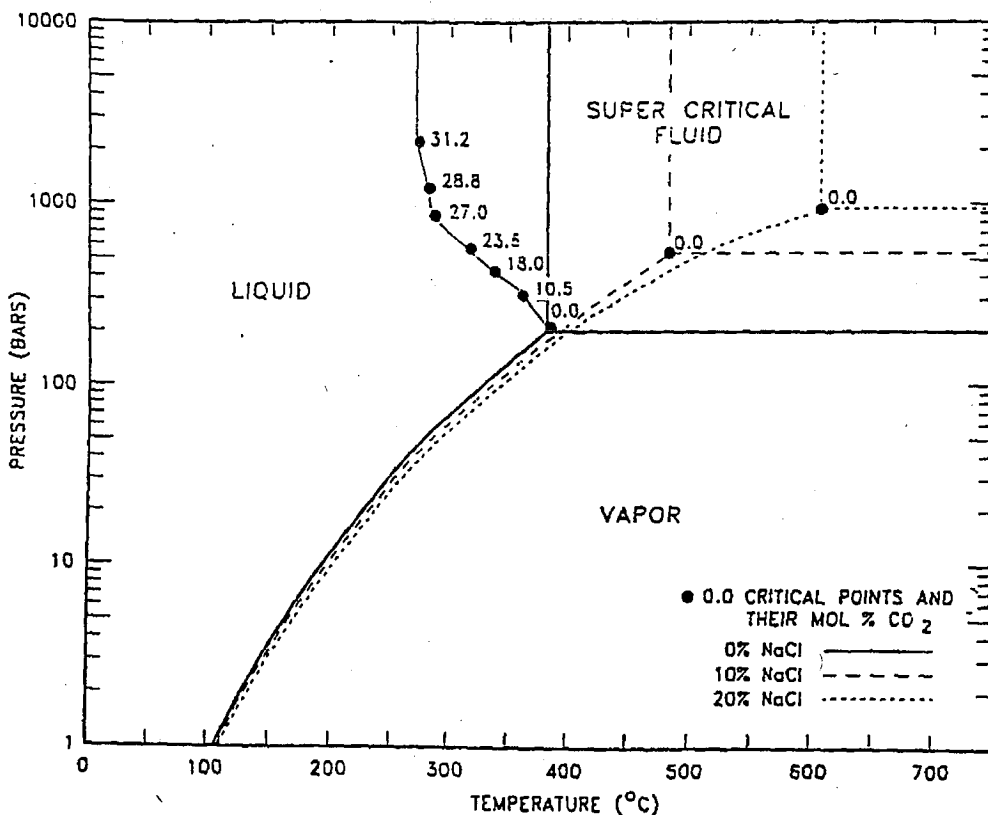


Figure 1. Pressure-temperature diagram showing phase relations and critical points for pure H<sub>2</sub>O (heavy solid lines), CO<sub>2</sub> in solution with H<sub>2</sub>O (solid circles on light solid line refer to critical points at denoted CO<sub>2</sub> mole fractions), 10 wt% NaCl solution with H<sub>2</sub>O (dashed lines), and 20 wt% NaCl solution with H<sub>2</sub>O (dotted lines). Diagram is based on experimental data reported by Haas (1976), Sourirajan and Kennedy (1962), and Takenouchi and Kennedy (1964).