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A reaction mechanism for tar decomposition at moderate temperatures with any coal type



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ABSTRACT

This study introduces the first detailed reaction mechanism for coal tar decomposition at moderate temperatures under nonreactive atmospheres; validates the mechanism with accurate interpretations of laboratory tests with diverse coal types; and develops a two-step global reaction scheme to mimic the predictions from the full mechanism in process design applications. Homogeneous tar decomposition reflects two conversion channels: (i) continuous elimination of heteroatoms as noncondensables, which transforms primary tar into polynuclear aromatic hydrocarbons (PAH); and (ii) disintegration of tar monomers with attached hydrogen sources into oils and additional noncondensables. The two conversion channels are coupled by a requirement that monomers disintegrate into oils only if they still have attached peripheral groups to transfer hydrogen into the oils, since the elimination of peripheral groups is a major pathway to eliminate oxygen and hydrogen from primary tar. The aromatic nuclei, labile bridges, char links, and peripheral groups in FLASHCHAIN[®] comprise a suitable basis set of structural components to describe tar decomposition, without modification. Five of the six proposed reactions were also transferred from FLASHCHAIN[®] without modification. Only the channel for oil production is new and distinctive in tar decomposition. All stoichiometric coefficients and all but two activation energies in the proposed reaction mechanism can be evaluated from FLASHCHAIN[®]'s submodel for coal constitution, which requires only the proximate and ultimate analyses for the parent coal. The analysis accurately predicts the reduction in the tar mass, oil yield, and enhancements to the yields of noncondensables for any coal type, given the coal properties and operating conditions.

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1. Introduction

The first step in any coal utilization technology is primary devolatilization, which spontaneously releases a mixture of light noncondensable gases (CO, CO₂, H₂O, H₂S, HCN, H₂, C₁–C₄ gaseous hydrocarbons (GHCs)); intermediate oils (benzene, toluene, xylene (BTX) and phenol, creosol, xylenol (PCX)); and a complex mixture of high-molecular weight organics collectively called tar. Primary tars often comprise as much as one-third of the organic coal components, including up to 40% of coal-O, 40–50% of coal-S, and disproportionate shares of coal-H. All volatiles continue to react once they escape their parent fuel particles unless they are immediately quenched to much cooler temperatures. Tars spontaneously release their heteroatoms as noncondensable gases, including fuels (CO, H₂, GHCs, oils) and pollutant precursors (HCN, H₂S). While tars are fully transformed into mixtures of polynuclear aromatic hydrocarbons (PAH) at moderate temperatures, the accompanying

additions to the distribution of noncondensable gases affect the reforming chemistry in gasifiers, especially at moderate-to-low temperatures, and also NO_x production in fluidized coal combustors.

Despite extensive characterization of tar decomposition at moderate temperatures in laboratory studies [1–9], no kinetics for tar decomposition have yet been reported, so this chemistry has not yet been incorporated into design simulations for coal utilization technologies. The FG-DVC pyrolysis mechanism contains an option that allows primary tars to continue to lose their functional groups in the vapor phase surrounding the fuel at the same rates applied in the condensed coal phase [10], which is fundamentally incorrect. This approach interpreted reported distributions of noncondensable gas products from an entrained flow reactor [11], where primary tars are quickly exposed to gases that are hotter than their parent particles. Both tar cracking into unsaturated GHCs and repolymerization of tar into soot were omitted from this analysis, even though the acute thermal severity in the tests would surely have converted all refractory components of primary tars into soot.

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Nomenclature

A	scaled molar concentration of aromatic nuclei in tar	p_T^b	probability for an intact labile bridge among nuclei in tar
A_i	pseudo-frequency factor in a reaction involving species i , s^{-1}	p_T^e	probability for an intact peripheral group on the end of tar fragments
A_T	pseudo-frequency factor for secondary tar destruction, s^{-1}	S	scaled molar concentration of peripheral groups in tar
1A_T	pseudo-frequency factor for primary tar production, s^{-1}	T	scaled molar concentration of tar fragments
B	scaled molar concentration of labile bridges in tar	t_j	tar fragment with j monomer units
b_i	stoichiometric coefficient for product i for oil production	$^1W_T(t)$	instantaneous yield of primary tar, daf wt.%
C	scaled molar concentration of char links in tar	$^1W_T^\infty$	hypothetical ultimate yield of primary tar, daf wt.%
E_i	activation energy in a reaction involving species i , kJ/mol	ΔW_T	difference between the instantaneous yields of primary and secondary tar, daf wt.%
E_T	activation energy for secondary tar destruction, kJ/mol	ΔW_T^∞	hypothetical ultimate difference between the yields of primary and secondary tar, daf wt.%
1E_T	activation energy for primary tar production, kJ/mol		
$f(E)$	distribution of activation energies in a DAEM-based process	<i>Greek Symbols</i>	
G	scaled molar concentration of noncondensable gases from tar decomposition	η	average moles of nitrogen per aromatic nucleus
J^*	maximum extent of depolymerization in tar fragments	v_B	scission selectivity coefficient for bridge conversion
k_i	rate constant for a reaction involving species i	v_C	stoichiometric coefficient for gas production during spontaneous charring
M_n	number-average molecular weight of tar, g/mol	v_O	stoichiometric coefficient for gas production during oil production
MW_i	molecular weight of species or component i , g/mol	σ_i	std. dev. about the mean energy for a reaction involving component i , kJ/mol
O	scaled molar concentration of oils from tar decomposition		
p_T	probability for any type of connection among nuclei in tar		

This paper introduces a phenomenological reaction mechanism for tar decomposition for any coal at any operating conditions, provided that the coal is heated fast enough to eliminate tar conversion inside the fuel particles and that temperatures are moderate. It first introduces the proposed reaction scheme and its implementation in FLASHCHAIN[®] theory, then covers several comparisons to laboratory datasets. Finally, a global reaction scheme for implementation in CFD and other process design applications is developed from the full reaction mechanism.

2. Mathematical analysis

2.1. Phenomenology

We focus on spontaneous tar conversion within mixtures of coal volatiles, as occurs naturally in coal pyrolyzers and gasifiers at moderate temperatures. All chemistry among noncondensable species is omitted, even though such chemistry certainly occurs with tar conversion whenever O_2 is present, and when H_2 is present at elevated partial pressures, and even when nominally inert volatiles mixtures are maintained at temperature. The reason for this omission is that elementary reaction mechanisms are already validated and available to easily simulate the chemistry of mixtures of the organics with single-ring compounds and lighter species, including pollutant formation. Indeed, phenomenological tar conversion chemistry represents a bridge from phenomenological reaction mechanisms for primary devolatilization to the phenomenal knowledge-base on hydrocarbon combustion chemistry developed during the last 50 years. This bridge has already been traversed for various applications at elevated temperatures where tar conversion is instantaneous [12–14], and the present analysis enables this approach at low and moderate temperatures. Soot production is relegated to a future extension, which restricts the mechanism to 800–900 °C, depending on hot-zone transit times. Heterogeneous tar decomposition from a free stream on char or

other reactive solids is also omitted. The proposed mechanism therefore describes the continuous elimination of C/H/O/N/S from primary tars throughout their transformation into PAHs plus the additional amounts of CO, CO_2 , H_2O , H_2S , HCN, H_2 , GHCs, and oils.

2.2. Tar constitution

The feedstock into the analysis is a stream of primary tars from rapid primary devolatilization. In abstract terms, primary devolatilization is easily distinguished from secondary chemistry: Primary devolatilization is the result of chemistry within the condensed coal phase, whereas secondary chemistry occurs in the gas phase beyond the interfacial area around the condensed phase. Even though the interface between the condensed and vapor phases is conceptually well-defined, numerous ambiguities still arise in practical applications. This analysis assumes that primary tars were generated at heating rates so fast that their transit time to the external particle surface was too short to sustain any tar decomposition during transport. The threshold heating rate is about 1 °C/s for the sizes and temperatures in common coal utilization technologies. Primary tars may spontaneously react as soon as they are released into an ambient stream if the temperatures are sufficiently high, or they may be transported at cooler temperatures into a second, dedicated environment for their sequential decomposition.

In the proposed tar conversion mechanism, tars' macromolecular structure is rendered in terms of the structural components of FLASHCHAIN[®] [15] as a mixture of chain fragments ranging in size from a monomer to a specified degree of polymerization, J^* . The diverse assortment of structural components in real tars is rendered coarsely with the same four structural components used for the parent coal: aromatic nuclei (A), labile bridges (B), char links (C), and peripheral groups (S). The model is formulated in terms of scaled molar concentrations, in units of moles per volume

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