

ADVANCED ENERGY SYSTEMS AND FUEL PROCESSING:
INTRODUCTION AND OVERVIEW
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Advanced Energy Systems and Fuel Processing: Introduction and Overview

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Fossil fuels, i.e., natural gas, oil and coal have been the mainstay of the economic well being of industrial and industrializing countries for much of the last two centuries. Their significance as primary energy sources as well as feedstocks for conversion to liquid hydrocarbons and further upgrading to petrochemicals, has constituted a strong incentive for the development of chemical engineering as a mature discipline. In 1970's and 1980's, the Organization of Petroleum Exporting Countries' (OPEC) pricing and production quotas highlighted the fragile dependence of the economic well being of many industrial nations on the availability of competitively priced oil, and resulted in increased and continuing global efforts towards energy diversification and conservation programs. Environmental issues of energy use such as toxic chemical and acid rain emissions, destruction of the ozone layer and global (greenhouse) warming promise to be the major focus in the remainder of this and the early 21st century. Despite the impending concerns over our environment, there will be a continuing reliance on fossil fuels as the most abundant, concentrated and cost effective global energy source. The focus will therefore shift towards technical fixes of a preventative or control nature to mitigate the overall environmental impact of fossil energy use. The increased costs will spur R&D aimed at developing alternative energy sources, particularly those of a renewable or sustainable nature. Within the matrix of fossil energy types, the relative ranking of natural gas as the environmentally cleanest fuel will favour its increased use over oil and coal. However, the greater abundance of coal may favour its increased use relative to natural gas and oil, provided that the overall cost of measures to minimize the environmental impact of coal use is more than offset by its lower market value relative to natural gas and oil.

Among industrial nations, Canada occupies a relatively unique position in possessing abundant fossil fuel and biomass energy resources. The articles featured in this thematic issue on 'Advanced Energy Systems and Fuel Processing' unabashedly reflect the R&D trends unique to the Canadian fossil energy and biomass resource base. However, despite this bias, we are fortunate in attracting contributions from other countries, notably the USA, Federal Republic of

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Germany, the Netherlands, France, Greece and Italy, demonstrating that the concerns over energy recovery and utilization issues are global.

Papers in the thematic section have been arranged according to the following broad topic groups:

- i) Heavy oil recovery and processing.
- ii) Combustion, gasification and pyrolysis of coals.
- iii) Hydrocarbons from natural or synthesis gas.
- iv) Biomass pyrolysis.

The section on **heavy oil recovery and processing** begins with a review paper by Butler comparing oil recovery from horizontal wells with conventional, vertical wells. Evaluation of the mechanics of vertical well production methods clearly shows that production rates diminish significantly with an increasing oil viscosity, as is typical for heavy oils and bitumens. By contrast, the recovery rates from horizontal wells are much higher for viscous oils due to a greater well exposure within the oil reservoir. Pressure drawdowns as small as one fiftieth of those for conventional wells as well as greatly reduced coning problems with a much lower co-production and use of displacing fluids, are demonstrated. Yields of 150 m³/d seem feasible for horizontal wells in steam assisted gravity drainage and with a well spacing of the order of 4 hectares.

The next paper by Ulrich *et al.* addresses the issue of bitumen separation from tar sands via solvent extraction, which is said to avoid the problems associated with the accumulation of clays in the process loop when using hot water. The technique is better suited for sands that do not possess a water film between sand and bitumen. The rotating disk immersed in fluid was chosen to study bitumen dissolution in organic solvents, since its geometry results in steady-state hydrodynamics and mass transfer characteristics which are constant with position at the solid-liquid interface and can be predicted quantitatively from first principles. The experimental data obtained show that the dissolution rate is a weak function of the bitumen's miscibility in a particular solvent, but is a stronger inverse function of the solvent viscosity. The use of the basic interphase mass transfer rate equation (coefficient times a concentration driving force) is not suitable for design calculations for bitumen contactors. A suitable model should take into account the gradual change in viscosity of the bulk solution.

The relationship between chemical structure and reactivity of bitumen and heavy oils is crucial to the understanding of product distribution derived from thermal and catalytic hydrocracking. The paper by Gray *et al.* represents an effort to find suitable reactivity markers with which to correlate

the conversion of the long residues (424°C+), obtained from topping operations during typical catalytic hydrocracking conditions. The most significant marker of processability was the conversion of the 525°C+ residue, which varied between 55 and 68%. This conversion correlated well with the average molar mass and the fraction of the α -carbon in the feed. The kinetics of residue removal were also used as comparison of reactivity between the four feeds. The first order pseudo-kinetic constant for the residue conversion showed a decrease with increasing average molar mass, contrary to the expected trend which suggests the opposite behaviour during thermal cracking. The asphaltene content was not useful as an indicator of processability. The sulphur removal as well as demetallization (Ni and V) and MCR correlated well with residue conversion, since the predominant mechanism of removal is thermal, but denitrogenation did not follow any regular pattern. Their study points out that interconversion of the produced fractions takes place and that a proper combination of distillation and structural analysis is required to shed light on the hydrocracking mechanism. The authors also conclude that an estimate of the hydrogen uptake is a useful indicator of reactor performance.

A paper centered on catalytic desulphurization of a model compound, benzothiophene, is next presented by Ng and Walker. The topic is of interest since it addresses the question of the relative roles of donor solvent and molecular hydrogen in desulphurization. A thorough application of statistical analysis and fractional factorial design (2^{n-1} , where $n=5$) is used by the authors to study the desulphurization mechanism. Catalysts for desulphurization are Mo and Co naphthenates and the variables considered are temperature, pressure, type of atmosphere (N_2 or H_2) and solvent (tetralin or *tert*-butyl benzene). Mo proves superior to Co for the hydridesulphurization of benzothiophene within the range of conditions used. The results show that molecular hydrogen is more effective than donor solvent hydrogen in the desulphurization process, in agreement with thermodynamic predictions. Mechanistic considerations have led the authors to conclude that desulphurization takes place through dehydrogenation to form dehydrobenzothiophene and subsequent bond rupture via hydrogenation resulting in H_2S formation.

The section on **combustion, gasification and pyrolysis of coals** begins with two papers on the use of circulating fluidized bed combustors. Among coal combustion techniques, fluidized beds have emerged as a preferred option due to advantages of in situ sulphur removal by in bed sorbents and the low NO_x emissions (principally NO and NO_2) arising from the low fuel combustion temperatures (typically $< 900^\circ C$). Typical efficiency gains in the conversion of coal to electricity may be 6% or more relative to a pulverized coal-fired power plant using flue gas desulphurization and $deNO_x$ equipment. Relative to bubbling beds, circulating beds also achieve much higher thermal heat release rates which provide a greater degree of operating flexibility and

simplify reactor scaling when using coals with a high ash content and/or low ash fusion temperatures. However, more recent data on the performance of fluidized bed combustors appear to indicate that low temperature combustion releases higher than normal emissions of nitrous oxide (N_2O), a direct greenhouse gas. Because its accumulation in the stratosphere is also harmful to the ozone layer, greater attention must be focused on reducing the level of N_2O emissions.

In their study on the circulating fluidized bed combustion of a high sulphur Eastern Canadian coal, Brereton *et al.* show that the capture and recycling of fine particulates are crucial to carbon burnout, in reducing the formation of calcium sulphide in the spent sorbent (a potential solid disposal hazard) and in increasing the overall level of sulphur capture at a given Ca:S sorbent molar ratio. The authors show that due to a possible catalytic effect, NO_x emissions increase with the Ca:S ratio. This highlights the need to minimize the level of sorbent utilization to reduce NO_x emissions and the tendency to form calcium sulphide from the reduction of calcium sulphate by excess lime present in the system. In comparing the results from their pilot scale unit with much larger utility-scale combustors, the authors emphasize the critical influence and differences in the solids residence time and the suspension density profiles within the combustor.

The second paper on circulating fluidized bed combustion of coal char by Arena *et al.* compares experimental data with theoretical predictions of combustion behaviour. The proposed models account for carbon surface reaction, intraparticle and external diffusion and char attrition. The performance of the riser portion of the reactor is tested by a comparison of the measured and predicted axial oxygen concentration profiles, the carbon content and char particle size distribution. The overall comparison shows a remarkably good agreement when external diffusion in the dense region of the reactor is assumed to be the rate controlling step for char combustion. A parametric test of the model shows that attrition rates make an insignificant contribution (<5%) in the improved prediction of char combustion behaviour, but this result may be different for other coal derived chars with a higher rate of attrition, a lower intrinsic char reactivity or a coarser feed distribution. Because the external diffusion limited model assumes that the coarse particle clusters in the dense phase are as large as the combustor riser diameter, further testing with larger scale units is recommended to verify the proposed model.

The third paper by Furimsky *et al.* looks at the distribution of volatile sulphur species during the pyrolysis and gasification of sub-bituminous and bituminous coals in a fixed bed reactor. The results show that pyrolysis and gasification releases sulphur mainly as H_2S with more minor concentrations of SO_2 and COS . The bulk of the H_2S evolution occurs during coal devolatilization and originates from the organic and inorganic matter in coals. For the latter, it is suggested that

sulphur is released mainly by the decomposition of pyrites, followed by reaction of the sulphur radical with hydrogen atoms removed from organic matter during pyrolysis or from steam in the gasification mode. The potential for the retention of H_2S by CaO present in the coal mineral matter is examined, with the conclusion that the reaction equilibria for CaS formation is unfavourable in the presence of a high steam concentration. Two of the coals showed a surprising and unexpected evolution of SO_2 during pyrolysis in a nitrogen stream. It is suggested that this release of SO_2 may be due to the oxidation of H_2S by oxygen chemisorbed by the coals during weathering. COS formation was found to occur mainly in the gasification mode. It is proposed that the reaction of H_2S with CO or CO_2 was the primary mechanism of COS formation under the gasification conditions investigated in their study.

The paper by Houzelot *et al.* deals with the flash pyrolysis of coal in a cyclone reactor. This configuration has the conceptual advantage of imparting a thermal shock to the particles and efficiently quenching the reaction products, thus limiting the extent of secondary reactions. The cyclone reactor behaves as a transport reactor and yet it improves the heat and mass transfer rates of the latter. The difficulties associated with the cyclone reactor are operational and result from an imprecise knowledge of the solids temperature and the necessity of steady fluid-dynamic regimes. The paper is an attempt to model the flash pyrolysis of a typical French coal by introducing into the fluid-dynamic model the kinetics obtained independently from the controlled pyrolysis of spherical coal particles based on classical quasi-stationary models. The resulting kinetics are only used as an approximation to model the conversion of the coal particles in the cyclone reactor. The fluid-dynamic models used by the authors are able to predict rather closely the conversions observed during flash pyrolysis in the cyclone reactor. The authors conclude that the operation of the reactor can be carried out in a kinetically controlled regime with a clear advantage when the coal is pre-oxidized prior to pyrolysis.

In the section on the production of higher **hydrocarbons from natural or synthesis gas** (CO and H_2), two papers are presented on the direct oxidative coupling of methane, while a third examines kinetic models for the conversion of a synthesis gas using a bifunctional catalyst. These studies are linked to the search for alternative production routes for liquid fuels and chemicals from natural gas, coal or biomass. The first paper on the oxidative coupling of methane by McNamara *et al.* looks at catalyst development. Specifically, the study examines the role of Nb_2O_5 and ZrO_2 as performance promoters in ternary and quaternary catalysts derived from Li/MgO and Li/Na/MgO . The addition of these oxides was found to improve catalyst selectivity and the capability to attain optimal C_{2+} yields at lower reaction temperatures. For the quaternary catalysts based on Li/Na/MgO , the catalysts also remained operative at higher reaction temperatures. In all cases, the

degree of enhancement in catalyst performance was also compared with materials derived from the alternative use of SnO_2 and Co_3O_4 as promoters. Among the suite of catalysts investigated, the Li/Co/MgO ternary catalyst showed the most significant change in the C_{2+} selectivity at temperatures $< 700^\circ\text{C}$. Ageing experiments were also undertaken with Li/Co/MgO in an untreated form, with pretreatment in CO_2 and under periodic dosing with CHCl_3 . Although the basic Li/MgO system is one of the most promising catalysts for this reaction, significant progress has yet to be made in achieving higher C_{2+} selectivities and yields necessary for process development.

The second paper on the oxidative coupling of methane by Andorf *et al.* presents results from a study on catalyst performance in a bubbling fluidized bed. Due to the high exothermicity of the oxidative coupling reaction, the reactor configuration necessary to maintain uniform temperatures is a key issue for process development. When using fluidized beds, agglomeration and attrition of the catalyst and the impact of bed hydrodynamics on catalyst selectivity and yield are the major developmental issues. In their work with the $\text{Na}_2\text{CO}_3/\text{CaO}$ catalyst, agglomeration in the dense phase was overcome by admixing $\alpha\text{-Al}_2\text{O}_3$ particles, whereas with the $\text{PbO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, high fluidization velocities ($U/U_{mf} \sim 15$) were used to overcome surface adhesion of the catalyst particles. However, the admixed material and the increased levels of gas backmixing at high fluidization velocities contributed to a reduced selectivity of the catalysts. Low methane to oxygen ratios in the gas stream were also found to reduce the C_{2+} selectivity and to increase the product yields. In all cases, the ethylene to ethane ratio in the product was found to increase significantly with the reactor temperature. In terms of the optimum performance for the coupling reaction in a bubbling fluidized bed, the highest selectivity and yield of C_{2+} , at 70% and 11.3%, respectively, were obtained for the $\text{PbO}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

The final paper in this section by Simard *et al.* looks at the kinetic modelling of a one step, synthesis gas to gasoline conversion using a $\text{ZnO}/\text{CrO}_3/\text{ZSM-5}$ bifunctional catalyst. Analysis of their experimental data showed that the synthesis route could be represented by the following main reactions; methanol synthesis from CO and H_2 , the conversion of methanol to higher hydrocarbons and the water gas shift reaction. Under the experimental conditions selected for their study, it was further established that the water gas shift reaction was in equilibrium and the methanol formed by the process was rapidly converted to higher hydrocarbons. Thus, the kinetics of methanol synthesis became the rate limiting step, and the overall reaction scheme could be modelled well by kinetic rate equations in which the methanol dependent terms were neglected and when the rate equations included a term linked to the fugacity of CO_2 ; the latter representing the inhibitory role of CO_2 on the methanol synthesis reaction.

The final paper by Koufopoulos et al. focusses on the modelling of **biomass pyrolysis**. The basic issue discussed in the paper is the coupling of chemical reactions with transport phenomena, in particular, heat transfer, for biomass particles treated in pyrolysis reactors at slow heating rates. It is assumed that the particles maintain structural integrity and that intraparticle heat transfer occurs by conduction only. A simple power-law expression represents the overall primary conversion of the biomass to volatiles, gases and char, whereas the secondary reactions between char and primary volatile and gaseous products are assumed to follow first order kinetics. Differential heat and mass balances are then developed which include the kinetics as well as the transfer rates; the conductivity and specific heat of the solid are functions of conversion. The model is applied to small sawdust particles and to large wood cylinders ($d=20$ mm) and predicts well the extent of biomass conversion (weight loss) for both sizes of particles. For the former, pyrolysis is controlled by the primary decomposition reactions whereas for the larger particles heat transfer is predominant, particularly at high pyrolysis temperatures.

