

GAS CRACKING CHARACTERISTICS IN THE COMMERCIAL RANGE OF OPERATIONS. R. Orriss, G. B. Nowowiejski and A. P. Moore. The M.W. Kellogg Company, 3 Greenway Plaza East, Houston, Texas 77046.

The cracking of gases for ethylene production has undergone a resurgence in recent times in the U.S.A. Prices for ethane have truly made it the feedstock of opportunity. Ethane continues to be of great interest as a feedstock in areas which have large gas reserves, among these being Canada, Indonesia, Nigeria, etc. Cracking conditions for ethane and propane require some interesting evaluations evolving from the unique situation with gases whereby unconverted feedstock is recovered as a pure product and can be recycled. The recycling of unconverted feed impacts the recovery section capacity and the ultimate yield of products obtained. This paper will show how the selection of severity is influenced by the values placed on feed, capital and by-products, for pure feeds and mixtures of ethane and propane. In designing new plants, the designer must also consider the effects of contact time and partial pressure. This paper will also look at the basic variations which affect capacity and ultimate yields as partial pressure and contact time are varied over the practical ranges achievable in commercial operations.

IMPLICATIONS OF FEEDSTOCK FLEXIBILITY IN THE DESIGN OF OLEFINS PLANTS. Stephen DeHaan. C-E Lummus, Combustion Engineering, Inc., 1515 Broad Street, Bloomfield, New Jersey 07003.

Currently operational olefins plants crack feeds ranging from ethane to vacuum gas oil. Until recently, most individual plants were designed to utilize a single feed. Even plants with some feedstock flexibility were usually based on either natural gas derived feedstocks or crude oil based feedstocks. Current and predicted future market forces dictate that new plants have considerably more flexibility. To assess the impact of feedstock flexibility on overall plant energy consumption and capital costs, a selection of case studies are analyzed.

OPTIMAL CONTROL OF AN OLEFINS PLANT. M. D. Weiss, Bechtel Petroleum, Inc., Houston, Texas 77001-2166

Within the past five years improvement in microprocessor computer control of Olefins Plants have enabled realization of numerous benefits in economy and energy savings in these facilities. The use of advanced control facilitated by microprocessor distributed control made optimization and control of pyrolysis furnaces, distillation columns, dryers, and other unit operation readily available to the ordinary control engineer, using environmental variable control, material balance control, heat balance control, energy minimization, and pollution control. Details will be supplied of control techniques used in the pyrolysis furnace, demethanizer system, acetylene removal and methyl acetylene/propadiene removal reactors, depropanizer, various driers and distillation columns, resulting in cost and energy savings, and in better control when the plant is operated at reduced capacity.

REACTOR SURFACE EFFECTS DURING STEAM PYROLYSIS OF A WHOLE CRUDE. C. W. Chang and B. L. Crynes. School of Chemical Engineering, Oklahoma State University, 423 Engineering North, Stillwater, OK 74078.

The thermal decomposition of an Alaskan crude oil in the presence of steam was studied in unpacked, downflow reactors. The experiments were conducted at essentially atmospheric pressure over a temperature range of 650-800 C with a mass ratio of oil-to-steam of 2.5. Four different reactors; 304 ss, alonized 304 ss, Vycor and Inconel 600, were chosen to study wall effects. The products from the pyrolysis reactions were lumped into three distinct entities: (i) a heavy liquid fraction boiling in the range of 210-550 C, (ii) a light liquid fraction from C_4 to boiling point of 210 C, and (iii) gas plus coke.

A model of reversible series reactions was postulated to fit the experimental data, and successfully predicted the trends of conversion and yields. The different surfaces showed varying effects on product distributions and coke formation.

FLASH PYROLYSIS PROCESS FOR THE PRODUCTION OF CHEMICALS AND FUELS FROM BIOMASS. Muthu S. Sundaram, Meyer Steinberg, and Peter Fallon, Process Sciences Division, Department of Energy and Environment, Brookhaven National Laboratory, Upton, NY 11973.

The objective of the work is to produce transportation fuels and chemical feedstocks from Biomass via Flash Pyrolysis. Experiments were conducted with oven-dried, saw-dust of Douglas Fir wood in a downdraft, continuous flow, bench scale reactor. The pyrolysis-gasification of wood particles was done in one step with no use of catalysts. The influence of various gaseous environments - which include hydrogen, helium and methane - on the reactivity of wood was investigated. The combined effects of high heat-up rate ($10^4 - 10^5$ °C/sec) of the wood particles and short residence times (0.5 - 4 sec) of the devolatilization products resulted in an almost complete gasification of carbon (99% C) in the feed wood at 850°C and 50 psi hydrogen pressure. Pyrolysis in methane was characterized by high yields of ethylene (up to 21% C) and BTX (up to 12% C). The effects of various pyrolysis atmospheres and major process variables on the yield and distribution of products were studied in detail. The composition of pyrolysis tars and basic kinetic data were also obtained. Preliminary economic analyses for the production of pipeline gas and methanol and chemical feedstocks have been made.

GAS EVOLUTION DURING PYROLYSIS OF CHATTANOOGA OIL SHALE R. J. Feng and M. D. McKinley. Chemical and Metallurgical Engineering Department, The University of Alabama, P. O. Box G, University, Alabama 35486.

A composite sample of Chattanooga oil shales from several counties in the states of Alabama and Tennessee was pyrolyzed in a nitrogen atmosphere to 990°C at three heating rates; 2, 5, and 12°C/min. The nonisothermal pyrolysis processes were carried out either without temperature soaking or with 10 hours isothermal soaking at 230°C. The oil shale particle sizes examined were -3+4 mesh and -8+16 mesh. A first order kinetic rate equation was used as the nonisothermal kinetic model in this study. Two kinetic parameters, frequency factor and activation energy, were evaluated by fitting the model kinetic equation to the gas evolution data using a nonlinear least squares program. The major gases identified in the pyrolysis gas include hydrogen, carbon monoxide, methane, carbon dioxide, ethene, ethane, and propane. The oil yield increased from 31.88 % to 54.79 % of the modified Fischer Assay as the heating rate changed from 2 to 12°C/min. The total volumes of gaseous products decreases from 85.68 cm³/g raw shale to 36.23 cm³/g raw shale when the heating rate increased from 2 to 12°C/min. Generally, lower heating rates tended to shift the maximum gas evolution rate to lower temperatures. Soaking the oil shale particles isothermally at 230°C for 10 hours did not improve the oil yield in this study. The nonisothermal kinetic model used gave a good representation of the thermometric experimental data measured.

COAL ANALYSIS USING THERMOGRAVIMETRY. M. A. Serageldin and Wei-Ping Pan.

Thermogravimetric, TG, analysis is increasingly being used today to obtain kinetic data related to coal decomposition. However, this method is open to criticism on the basis that the meaning of the activation energy of solid state reactions obtained from TG experiments is not clear. In this study a linear relationship between procedural activation energy and enthalpy of reaction was found. This is typical of elementary reactions of atoms and small radicals. The effects of alkali metal salts on the decomposition of coal under three gas atmospheres (N_2 , CO_2 and air) were investigated. Several features were reported such as the effect of the catalysts on coal conversion and CH_4 , CO and CO_2 emission. These were related to observed changes in activation energy.

KINETIC INVESTIGATION OF LIGNITE PYROLYSIS. Jefferson Jih and Uzi Mann, Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409.

In this paper we describe an experimental method for determining the individual kinetic parameters (frequency factors and activation energies) for the formation of gaseous, liquid and solid products during lignite pyrolysis. The system constructed facilitates the collection of the gas and tar formed and measurement of the solid weight loss as a function of time. In addition, the technique facilitates monitoring the solid temperature with time. The latter enables one to account for the solid "heating-up" effect in determining the kinetic parameters.

The pyrolysis of San Miguel (Texas) lignite between 600 and 950°C was investigated. It was found at these temperatures the sum of all lignite decomposition reactions is exothermic. This is probably due to partial simultaneous oxidation of the lignite with structure oxygen. An attempt is described for estimating the pyrolysis rates constant by subtracting of the oxigenated gaseous carbon products from the total gas generated. Experimental kinetic data of Texas lignite are analyzed and the theoretical basis and computation procedures of estimating the kinetic parameters are discussed.

LIGNITE DEVOLATILIZATION IN A FIXED BED REACTOR. A. J. Gokhale and R. Mahalingam, Department of Chemical Engineering, Washington State University, Pullman, WA 99164.

Devolatilization of lignite coal with a steam/oxygen mixture in a fixed-bed, atmospheric pressure reactor, in the temperature range 300 C to 550 C, with the objective of studying the tars. The particle sizes were (-2+1), (-3+2) and (-4+3) mm. The tar yield was observed to increase and then decrease with temperature, due to secondary cracking reactions. The melting point, viscosity and specific gravity of the tar samples increased with increase in devolatilization temperature. A first order single reaction model, when fitted to the experimental data, yielded an energy of activation in the range 15 to 18 kcal/mol, irrespective of particle size. A series-parallel reaction model indicated that the cracking of tar to char kinetically represented the most difficult step.

PYROLYSIS OF WESTERN CANADIAN COALS IN A SPOUTED BED REACTOR. A. Jarallah and A. P. Watkinson. Department of Chemical Engineering, The University of British Columbia, Vancouver, B.C. Canada V6T 1W5.

Coal pyrolysis has been studied in a 12.8 cm dia. continuous spouted bed reactor with the aim of determining conditions for maximum liquid yields from Western Canadian coals. Nitrogen and nitrogen/carbon dioxide mixtures and coal of size - 3.36 + 1.12 mm are fed at atmospheric pressure to an electrically heated reactor containing sand. The tar yield is determined by sampling the outlet gas through a series of cooled impingers. The spouted bed pyrolyzer behaves in a manner similar to a fluidized bed unit, and shows a maximum tar yield with temperature at a fixed feed rate. At a given pyrolyzer temperature, the tar yield was inversely proportional to the coal feed rate over the range 0.4 to 7.6 kg/h. Coal type strongly influenced the liquid yields as expected. A bituminous coal (Sukunka) from the Peace River coal field gave a maximum tar yield at 600°C of 31% wt/wt MAF coal at a feed rate of 116 kg/hr-m². The corresponding gas yield was 2.8%, and the char yield (uncorrected) was 64%. At about the same throughput, a maximum tar yield of 19.4% wt/wt MAF coal at 580°C was found for Balmer coal - a bituminous coal from the Crowsnest coal field. A sub-bituminous coal, Forestburg, from the Edmonton Formation produced significantly higher gas yields of 20% versus 6% for the bituminous coals due to higher CO₂ production and a tar yield of 21% at 530°C. With Sukunka coal, a steady increase in tar yield from 20.4 to 22.4 to 26.7% wt/wt MAF coal was found as the average coal particle size was reduced from 2.28 to 0.95 mm to 0.65 mm. No significant effects on tar yield were found for variations in bed depth, or vapour residence time.