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THE SBRG CONTINUOUS FLOW COAL LIQUEFACTION TESTING FACILITY FOR DIRECT HYDROGENATION OF CANADIAN LOW RANK COALS

G. Teodosiu[1], R. Arsenault[1], G. Bellemore[1], E. Chornet[1,3], S.L. Hodd[1], J.F. Kelly[2]

1. Sandwell Beak Research Group, 6870 Goreway Drive, Mississauga, Ontario L6V 1L9
2. Energy Research Laboratories, Department of E.M.R., Ottawa, Ontario K1A 0G1
3. Also affiliated with Université de Sherbrooke, Sherbrooke, Québec J1K 2R1

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ABSTRACT

A 10 kg/hr continuous flow testing facility for direct hydrogenation of Canadian low-rank coals was recently commissioned by SBRG at its research centre in Mississauga. The research and development program leading to the construction of this PDU is presented. The scientific and technical aspects of the program were approached in two phases: an initial experimental statistical study using batch autoclave techniques in order to establish correlations of conversion and oil yield as a function of reaction parameters followed by the design, construction and commissioning of a continuous PDU. The design basis for the PDU was derived from the results obtained in the batch studies. A summary of the information obtained in the batch autoclave work using a Western Canadian lignite, comments on the design, construction, operational range, problem areas are discussed. Also preliminary results and mass balance for a specific case are presented.

NOMENCLATURE

AO = weight of anthracene oil, g
E = weight of benzene-free extract, g
F = weight of benzene-free filtrate, g
L = weight of moisture-free lignite, g
LTA = weight of ash in the moisture-free lignite, g
m.a.f. = moisture and ash free coal
PDU = process development unit
t = nominal contact time at reaction temperature, min.
T = reaction temperature, °C
Y_c = conversion, wt. %
Y_r = oil (benzene-solubles) yield, wt.%

INTRODUCTION

The operation of a process development unit for the liquefaction of Canadian low-rank coals is part of an on-going multi-year program supported by the Canadian Federal Government.

The long-term objective of the liquefaction program is to contribute to Canadian liquid fuels production through the definition, research development and demonstration of coal liquefaction technologies for the Canadian market place. Low rank coal processing was given an initial high priority in this program.

Despite their higher oxygen content, low-rank coals might become attractive as a feedstock for conversion into oils. As compared to high-rank coals, their reactivity is enhanced by the presence of humic structures which may act as hydrogen donors to stabilize free radicals intermediates. Consequently, a significant fraction of the original material can be rapidly converted resulting in improved space-time yields. As well, since carbon monoxide is beneficial for converting oxygenated coals, less expensive synthesis gas may be used rather than pure hydrogen. Finally, low-rank coals are easily minable and their cost low enough to be eventually attractive as feedstock for a conversion.

The main objective of the liquefaction program undertaken by SBRG with CANMET support involved two aspects, namely: establishing of the design basis for a process development unit as a step towards commercial production of coal derived liquid fuels in Canada and development of skill and expertise for design, construction and operation of a continuous flow coal liquefaction plant. The work undertaken to date was done using Western Canadian lignites and subbituminous coals. The scientific and technical aspects of the program were approached in two phases.

An initial program consisted of primary liquefaction of Saskatchewan lignite using batch autoclave techniques. A statistical study was conducted during the first year of the study. Correlation of conversion and oil yield as a function of temperature, pressure, contact time, carbon monoxide/hydrogen ratio were obtained. This work was continued in a second year program aimed at the enhancement of conversion and liquid yields by use of catalysts, simulation of continuous processing by use of reycle coal derived oils as a solvent. Also simple product upgrading tests were conducted.

The results obtained in the batch experiments confirmed the need for further investigation on a continuous PDU and provided the design basis for it.

In the second phase of the program, the design of a 10 kg slurry per hour PDU was accomplished. construction of the vessels, procurement of the equipment were carried out, the assembly and commissioning of the unit were finalized.

In what follows we will summarize the information obtained in the batch autoclave and describe the considerations that led us to the actual design. We will also comment on the modular concept used for the unit, its operational range, problem areas encountered in the construction, operation and monitoring of the equipment. Mass balances, product distribution for a specific test case will also be discussed.

STATISTICAL STUDY ON BATCH CONVERSION OF ESTEVAN LIGNITE

The objective of the batch autoclave work in our program was to provide a thorough parametric investigation of the hydrogenolysis of a Canadian lignite using CO and H_2 mixtures as reducing agent. The experimental variables studied were temperature, pressure, CO/H_2 ratio and contact time. The approach followed was based on a factorial design of experiments (2).

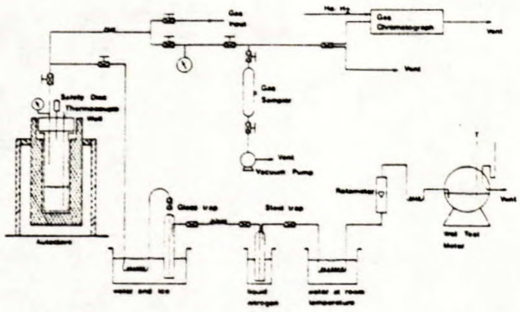
A first set of experiments without added catalyst were fitted to a statistical model using a partially replicated 2^4 factorial design. A second set focussed on catalytic deoxygenation and hydrogenation experiments using cobalt-molybdate, nickel and iron catalysts.

The experimental arrangement used for batch hydrogenolysis is shown in Figure 1. Each experiment consisted of mixing a known quantity of pulverized lignite (75% passing through a 200 mesh Tyler Screen) with anthracene oil at a solvent/m.a.f. lignite mass ratio of 2.8. The solvent oil was provided by Crowley Tar Co., Kent, Ohio. The mixture was sealed in a 1L Parr rocking autoclave made of Inconnel 600 alloy, and placed in a heating jacket. The contents of the autoclave were flushed with hydrogen. Carbon monoxide and more hydrogen were then introduced into the reactor to a specified initial cold pressure and composition.

The autoclave was then heated gradually (approx. 9°C/min) to the reaction temperature and agitated by rocking for a known time. At the end of the specified contact time, the mixture was cooled by withdrawing the autoclave from the heating mantle and by blowing air over the reactor. When the temperature was reduced to 105^oC, the reactor was replaced in the heating mantle and kept at this temperature during gas recovery.

The gaseous phase was vented through a series of coils and condensers to recover water and light oils, as shown in Figure 1.

Figure 1 - Batch Hydrogenolysis Apparatus.



The total gas volume vented was measured by a wet test meter and the final composition was determined with a gas chromatograph following established procedures (3).
The condensed liquid recovered in a trap immersed in ice water was weighed and stored in a sealed jar. This product consisted mainly of water and light oils.

The condensed material in a trap immersed in liquid nitrogen was vapourized at room temperature. The gas composition was monitored to detect the presence of light hydrocarbons and its volume measured by a wet test meter.

Immediately after venting the gases from the autoclave, the reactor was removed from the heating jacket and placed on a revolving support. The reactor head was removed and the condensed phase (the slurry) treated for recovery of the bitumen-like product. The liquid and solid products were poured directly into a Soxhlet extractor thimble and extracted with benzene in a Soxhlet apparatus. The residue, containing unextracted or unconverted components was dried, weighed and analysed.

The liquid extract was combined with the filtrate from the autoclave, and the mixture distilled in a rotary flash evaporator at 32°C and 150 torr to remove the benzene. The bottoms, containing oils, tar and anthracene oil, were weighed, sealed in a jar under Argon and stored for chemical analysis. Conversion Yc and oil yield Yr were calculated from the following relationships:

$$Y_c = 100 - \frac{100(R - LTA)}{L}$$

where R = weight of unconverted and unextracted residue
LTA = weight of ash in the m.f. lignite as determined by low temperature (440 C) ashing procedure
L = weight of m.a.f. lignite charged to the reactor

$$Yr = \frac{100(F + E - AO)}{L}$$

where F = weight of benzene - free filtrate
E = weight of benzene - free extract
AO = weight of anthracene oil charged to the reactor

Mass balances were calculated for each experiment.

The range of experimental variables studied was kept within convenient process conditions: 380° C to 460° C reaction temperature, 7.1 MPa to 11.1 MPa initial cold pressure, 10 to 50 minutes residence time at reaction temperature and 0.25 to 0.75 initial H_2 molar fraction in the gas. The conversions obtained within these ranges varied from 53.3 to 85.3% and the liquid yield varied between 24.6 and 63.4. Maximum conversion was obtained at 460° C reaction temperature, 11.1 MPa cold initial pressure and 3/1 CO/H_2 molar ratio. The highest liquid yield was produced at 380° C reaction temperature, 11.1 MPa cold initial pressure and 3/1 CO/H_2 molar ratio. The information obtained in this statistical study was further used in selection of the design basis of the continuous flow system.

Once the conditions for maximization of oil yield were determined, the next step was to attempt simulation of a continuous process by using recycle product as solvent. A very simple testing program was designed based on 5 passes through the process (4).

A simulated recycle oil was produced comprised of 50% oil derived from lignite liquefaction and 50% oil derived from anthracene oil treated under liquefaction conditions. When using this simulated recycle oil as carrier oil for lignite liquefaction, a decrease of benzene solubles yield occurred as compared to using raw anthracene oil as carrier. The oil yield obtained at the reaction conditions tested decreased from 48% to 40%.

The recycle oil had a higher oxygen content than the anthracene oil. The recyle operation would result from the processing viewpoint, in higher viscosity products than those derived from a once-through operation using anthracene oil. The poorer characteristics of the reycle oil as hydrogen donor resulted in a lower selectivity to oils and also favoured condensation reactions leading to a solid carbonaceous residue. A definite carbon enrichment of this residue was observed when recycle oil was used instead of anthracene oil.

In view of the reduced hydrogen donor properties of the recycle oil as determined from the lower oil yields during hydrogenolysis of lignite, an intermediate hydrogenation step of the recycle oil might be required for continuous operation, or a specific cut of this recycle oil might have to be used instead of the entire material. In view of these results, the experimental program on the continuous flow system will include recirculation of a specific cut of the coal-derived oil as solvent and a more in-depth study of the product obtained and process conditions related to recirculation of solvent.

CONTINUOUS FLOW LIQUEFACTION SYSTEM

The design basis selected for this system was the set of conditions at which maximum liquid yield was obtained in non-catalytic tests where lignite, anthracene oil and CO/H_2 mixtures were used (Table 1).

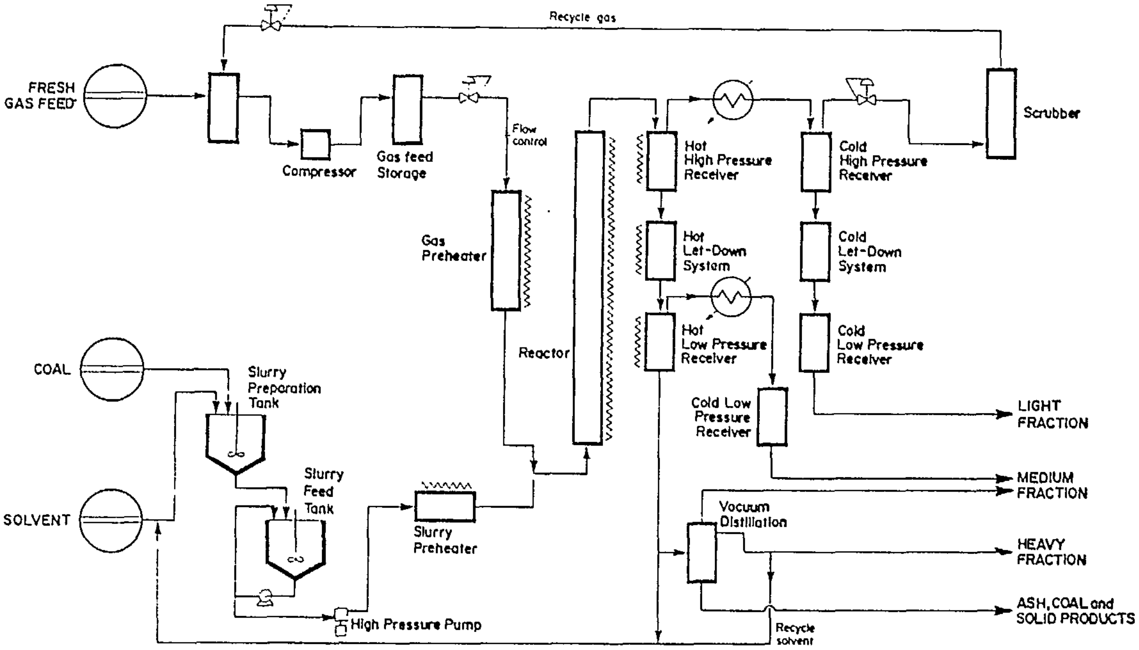
This PDU was built with two objectives in mind: a) to provide a system capable of operating safely for long periods of time at controlled conditions in order to produce data for scale-up to a pilot around 5-20 tonne/day; b) to have a testing tool adequate for characterization of various coals with respect to their potential as synthetic fuels feedstock. In order to achieve these two goals a great degree of versatility was built in, the design specifications and the flow sheet were carefully prepared to allow the monitoring of either one module only, or of the whole process in detail, allowing for calculation of mass and energy balances, appreciation of equipment performance and easy variation of process parameters.

Table 1: Design Specifications for PDU

Slurry feed rate	10 kg/hr
Gas feed rate	1200 m^3/t coal
Slurry preheat temp.	300° C
Gas preheat temp.	400° C
Reactor temp.	475° C
Reactor press.	31 MPa
Scrubber press.	4 MPa
Retention time at reaction temp.	60 min.

The unit was designed for a nominal capacity of 10 kg coal slurry/hour, maximum operating temperature of 475° C, maximum operating pressure 31 MPa, use of either syngas or pure hydrogen as reagent gas, recirculation of the gas after purification, recirculation of selected distillation cut to be used as oil carrier. The design concept was to use industrial or as close

Figure 2 Schematic flow diagram of the continuous flow coal liquefaction system



as possible to industrial type equipment in view of facilitating the scale-up step and obtaining of data required for an economic analysis.

The PDU was constructed in a high bay area, some of the vessels being situated on a beam-supported, grill-type deck at 12 ft. elevation. The rest of the system was supported on a vertical, welded steel profile frame, allowing for easy maintenance access, short slurry lines and full visibility of the whole system. All electrical conduits as well as the instrument panel are under positive atmosphere.

The material used for the construction of the system was stainless steel 316, for vessels, lines, valves and fittings. The only exception being the use of tungsten carbide in the main let-down valves and the check valves and piston of the high-pressure slurry pump. All high-pressure lines and vessels were provided with cone and thread connections. All slurry lines and vessels were heat-traced and insulated to ensure a temperature of 60-80°C at all times and so avoid line plugging due to solidification of the slurry.

The flow diagram of the PDU is presented in Figure 2. A modular concept was used in designing the system. Mass balances can be closed over each module and also changes can be made within each module without disturbing the others. The system can be regarded as a combination of 6 modules:

- slurry preparation and feed
- fresh gas manifolds
- reactor
- let-down and product collection
- gas scrubbing
- gas recirculation.

A batch operated vacuum distillation apparatus can provide the selected cut for the recirculation as carrier oil.

The slurry preparation module is comprised of a slurry preparation tank, provided with a multi-blade stirrer, electic heater and connection to inert gas and to the slurry feed tank. The loading of this tank is made batch-wise, each batch being enough for 8 hours unit operation at a feeding rate of 5 kg of slurry/hour. From this vessel, the slurry is transferred to the slurry feed tank. The construction of this tank is similar to that of the preparation tank, but for the purpose of feed rate monitoring, this vessel is suspended on a load cell. The slurry is continuously recirculated at a sufficient rate to keep the coal in suspension by a low-pressure recirculation pump. The slurry is heated under inert blanket at all times. A high-pressure piston pump takes suction from the recirculation line at a pressure of 50-70 KPa. The slurry feed rate can be changed by adjusting the stroke.

The fresh gas feed module includes a separate manifold for each of the following gases: hydrogen, carbon monoxide, nitrogen and and helium; each provided wth pressure regulators and flow meters. The fresh gas is supplied from commercially available cylinders. The flow of each individual gas is regulated by micrometric valves, the H_2/CO ratio can be varied to obtain the desired concentration after the combination with recycle gas.

The reactor module comprises the slurry preheater, the gas preheater, the upflow reactor, hot high-pressure receiver, the cold high-pressure receiver, the condenser and the backpressure regulator.

Each one of the components can be removed, bypassed, modified or replaced if the process requirements change. All the heaters are electric and temperatures are automatically controlled. The pressures are regulated by spring-loaded pressure regulators.

The slurry preheater is a coil imbedded in a heat transfer cement block, heated by a finger heater. The gas preheater is a larger diameter pipe, provided with stripe heaters. Temperatures in both preheaters are measured and regulated by the temperature of the fluid leaving the preheater.

The possibility of splitting the gas flow before and/or after the preheater is a built-in option serving a double purpose: to prevent slurry preheater coking in case of a temperature run in the preheater and to help cool the in-flowing slurry in either the preheater or the reactor in case of a temperature run in the reactor.

The reactor is an empty, upflow tubular reactor, built with modified high-pressure Bridgeman closures, provided with 4 heating zones, individually controlled by thermocouples placed directly in the flow.

The reaction mixture leaving the reactor at the reaction temperature and pressure reaches the high temperature, high-pressure receiver where the first flash takes place. The vessel is tubular, provided with the same type of closures as the reactor. The liquid level is kept constant with the help of a γ-ray level indicator.

The vapor phase comprised of unreacted H_2, CO, H_2O and produced CO_2, H_2S, NH_3, and low boiling hydrocarbons leave the hot high-pressure receiver at the top, go through a water-cooled condenser where the light fraction and the water are condensed and reach the cold high-pressure receiver. The non-condensed gases are separated at the top and led to the scrubber and the low boiling product containing water, some sulphur and ammonia products and light hydrocarbons are collected periodically.

The liquid phase from the hot high-pressure receiver is evacuated via the let-down module. The heavy product pressure let-down module is constituted of two separate trains, each comprising two sequentially operated on/off actuated valves with a small intermediate vessel in-between. The timing of the valves is manually adjusted, based on the indication of the γ-ray indicator, the feeding rate and reaction parameters.

The slurry stream can be directed on either of the let-down trains while the other one is completely isolated allowing eventual repair work to proceed.

The heavy liquid stream off the let-down system is collected in a hot receiver where the last of the dissolved gas, water vapors and products boiling lower than 200°C are leaving the liquid phase in the process of the pressure release, and after being cooled in a condenser the condensate is periodically collected and analysed as intermediate product..

The liquid phase evacuated hourly from the hot low-pressure receiver contains the ash and unreacted coal along with heavy product and recuperated solvent fraction. This mixture is subjected to vacuum distillation in order to separate the distillable product including the recycle solvent cut from the solids-containing residue.

The gas scrubber module was designed for operation at ambient temperature and 4 MPa. The scrubber itself is a packed column where the gas moves in counter current with the absorbing medium which can be water, caustic solution or methanol. The absorbent solution is circulated with a pump to the top of the scrubber and it is periodically analysed. The solution leaving the scrubber is kept in a closed tank connected to the exhaust system in order to allow the dissolved gases to escape.

The gas recycle module involves a scrubbed gas storage tank kept at max. 4 MPa by a system of spring-loaded pressure regulators. A diaphragm compressor takes suction from this tank and discharges the gas mixture at high-pressure into a buffer tank which serves as gas feed tank. The recycle gas composition is analysed hourly and calculated ratios of fresh make-up gases are added into the compressor's suction to achieve the desired H_2/CO ratio.

In its present configuration, the PDU can operate in a variety of modes due to particular built-in features which were included in the design in view of confering the great versatility required from a testing facility. Some of these capabilities have already been tested, some are part of the on-going research program in progress.

A complete coal testing program will include establishing the reaction parameters for optimum liquid yield, calculating conversion, total mass and energy balances, gas make and hydrogen consumption, distillable yield, slate of products and quality of discharged water, composition of exhaust gas and of residual solids.

The following conditions can be changed and their influence can be studied in relation to conversion of coal or liquid products yields:

- solids content in the initial slurry
- slurry feeding rate
- gas flow and gas/coal ratio
- initial gas consumption
- temperature of the feed
- temperature and pressure of the reaction module
- retention time at reaction temperature
- type and composition of the solvent
- temperatue of the hot high-pressure receiver
- temperature of the hot low-pressure receiver
- liquid flow through the scrubber
- retention time in the hot high-pressure receiver
- temperature and velocity of the slurry through the preheater
- once-through catalysts can be added to the coal or solvent.

Other types of processes that can be tested with minor or no modifications to the unit are: solvent hydrogenation, product upgrading, bitumen or heavy oil-coal co-processing both in catalytic and non-catalytic modes.

Testing at one given set of conditions implies operating the system at those conditions for enough time to satisfy the steady state condition after which data are collected for a period of 4 to 8 hours. The recorded data are: pressures temperatures in all critical points, liquid and gas flows in and out of the unit, gas composition in the gas feed storage tank, before and after the scrubber and in the gas exhaust lines.

For future development work our group is contemplating trying other types of reactors, gas purification systems and/or solid/liquid separation techniques.

Provisions were made in the design and assembly of the system to allow for installation of other reactors in parallel to the existing one.

One very important part of the effort put in building this system was dedicated to safety features that were included in the design. The room housing the PDU has been provided with a ventilation system capable of handling 40 air changes per hour. Continuous monitors of H_2 and CO were installed in the critical areas. All main valves are air actuated and the air supply to actuators was doubled with a N_2 supplied back-up system. The high-pressure pump and compressor have automatic cut-offs and high level alarms in addition to the usual safety relief valves. A 1/2 inch lexane barrier protects the operators in case of fire, splash due to connection failure or explosion; access behind the barrier is not permitted during operation. All manual valves have extended stems which allow manipulation from outside of the barricade.

Emergency procedures were established which permit the blow-down of the unit in case of equipment failure. Intensive personnel training was undertaken in safe working procedures.

This system was commissioned in 1981. Three test runs have been conducted with lignite and pure hydrogen. The results obtained are very encouraging in terms of equipment performance and problem-free operation. Continuous operation for periods up to 70 hours were achieved, during which 98% mass balance were obtained.

Using a Saskatchewan lignite containing 21% moisture and 13.6% ash, anthracene oil as carrier solvent and 98% hydrogen, at 425°C and pressure in the order of 21-24 MPa, the conversions obtained on the continuous system are in the order of 75-82%, liquid yields vary from 65 to 73%. These results are only preliminary and based on the batch testing results we expect to improve greatly the liquid yields by using a mixture of hydrogen/carbon monoxide instead of hydrogen.

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