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TECHNIQUES OF DIRECT COAL LIQUEFACTION, PHASE II

DP/CPR/83/002

Technical report: Separation and analysis of coal liquids *

Prepared for the Government of the People's Republic of China
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Khay Chuan Teo,
Consultant in coal science and modern analytical instrumentation

United Nations Industrial Development Organization
Vienna

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ABSTRACT

This report describes work carried out on behalf of UNIDO under the job description DP/CPR/83/002/11-53/32.1.1 for the 10 day period (November 21 to December 1, 1986) at Central Coal Mining Research Institute (CCMRI), Beijing, China. Five lectures on selective topics were given in Chinese (Mandarin) and brief lecture notes, slide and transparency presentations were in English. The five lectures (2.5 hours per lecture) covered the modern concepts of coal science, high resolution gas chromatography (HRGC), high performance liquid chromatography (HPLC), nuclear magnetic resonance spectroscopy (NMR), modern GC-mass spectrometric (MS) method with practical examples on coal derived liquid characterization, including analysis of hydrotreated liquids. Site visits included the three coal liquefaction continuous process units (CPU), the hydrotreating unit and all the major analytical facilities in operation. Discussion was held with three different research groups representing coal liquefaction study, analytical service and coal combustion study.

The Chinese Authorities highly appreciate the continuous support and coordination of UNIDO on the coal liquefaction program and funding for upgrading and modernizing their analytical service through state-of-the-art instrumentation. They also expressed great regard for the contributions and assistance from the participating countries Federal Republic of Germany, Japan, United States and others. They are working extremely hard with a good understanding on all the existing facilities. Technically, they are ambitious and doing extremely well. There is room for improvement. Identified areas are linked to the effective management of their own intellectual resources and means to improve better analytical service with higher utilization of the in-house analytical facilities. Allocation of extra funding for maintenance requirements and upgrading of the existing analytical instrumentation from time to time is also recommended.

ACKNOWLWDGEMENT

I greatly appreciate the effort of UNDP and UNIDO at Vienna and Beijing and the recommendation forwards by CCMRI of Beijing in providing the valuable opportunity for the consulting work. Special thank to the Director, Mr. Dai Hewu for his effort and his colleagues at Beijing Research Institute of Coal Chemistry. I express my deep gratitude.

K. C. Teo, Ph. D.
Senior Research Scientist

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CHAPTER I

INTRODUCTION

Evaluation of candidate coals for liquefaction characteristics in the three continuous process units (CPU) is the main objective of this United Nations Development Programme, entitled " **Techniques of Direct Coal Liquefaction, Phase II**". The details of this programme is contained in the project document CPR/83/002/A/01/37. The duration of Phase II is scheduled from 1985 to 1988.

The production of liquid fuels and coal based organic chemicals from the coal derived liquids to meet the China's energy demand and building a strong source of organic feedstocks for chemical industries are of vital importance to their industrial development. Although there is no immediate plan for commercialization, the Chinese Government foresees the importance of readily available of coal liquefaction technology on hand for their candidate coals in the year of nineties.

Evaluation on the competence of a liquefaction process as well as the potential of a chosen coal depends primary on the yield, qualilty and production cost of the raw liquid product under the most optimal conditions. The less problems with downstream handling and upgrading to the end-user products will justify the success. The assurance on the quality of the raw liquid product will have to subject to scrutiny chemical structural analysis and physical property characterization prior to the design or chosing of a suitable upgrading process.

With the funding make available to CCMRI from Chinese Government and the UNDP inputs, the institution has laid down a sound foundation in the area of essential analytical facilities and trained personnel since the commence of this programme.

The objective of this consultant work is part of the research programme to provide lectures in the selected areas of analytical methods suitable for coal liquid characterization and to evaluate the related problems and to identify areas that require attentions and improvment for better productivity outputs from the analytical service for the ongoing liquefaction programme.

CHAPTER II

SUMMARY OF LECTURES

A total of five lectures on five selected topics was agreed by the director Mr. Dai Hewu upon the arrived of the consultant. Each lecture last two and a half hours. Lecture and dialogue with the attendents were conducted in Chinese (Mandarin). Lecture notes, slide presentations and transparency overhead projections were given in English. As a matter of facts better communication efficiency was expected. The following Sections A to E outlined the contents in the five given lectures.

A. Modern coal chemistry

Current studies (mainly post-1970) from published literature results with focus on the following topics:

1. General introduction regarding the importance on the contemporary concepts of coal structure.

2. Physical property measurements of coals: types of physical properties and methods of determinations.

3. Standard laboratory test methods for coal and coke products (a brief summary).

4. Average molecular structure of coal: structural parameters, molecular weight of coal deducted from various chemical methods, the approaches used to solve the carbon aromaticity of coal, marcerals and coal products, the molecular ring structures derived from chemical degradation studies, the aromatic and aliphatic structures of coal, the nature of heteroatomic structure, guest molecules in coal, free radical in coal structure, the various macromolecular skeletal structural models.

5. Briefing on coal structure and contemporary coal rank classification.

B. Gas chromatography (GC) and high performance liquid chromatography (HPLC) in coal liquid analysis.

1. General introduction on high resolution (capillary) gas chromatography **(HRGC)**, choice of detectors for specific purposes, injection systems, other accessories, column selection, and specific examples on coal derived liquid analysis.

2. Advantages of high performance liquid chromatography (HPLC), the HPLC system, column selection guide and mobile phase selection, the injection system, choice of detectors, applications of HPLC on hydrocarbon group type separation for coal derived liquids.

C. Gas chromatograph-mass spectroscopy (GC-MS) for coal liquid analysis.

1. An introduction to the modern quadrapole mass spectrometer, including the followings: the quadrapole mass analyser; the EI and CI modes of operation; the GC and MS interface (cf. the molecular jet separator); total ion chromatogram and selective ion mass display.

2. Integrated examples from literatures on HPLC, HRGC and GC-MS with particular emphasis on the coal oil and coal asphaltene analysis.

E. C-13 Nuclear Magnetic Resonance (NMR) Spectroscopy

1. A brief introduction to C-13 NMR: The chemical shifts, coupling constants, additivity rules, the steric γ-effect, application examples in structural elucidation.

2. Current advancement in NMR: solid state NMR; imaging etc.

F. My current research work on coal

1. Rapid pyrolysis of Canadian coal in spouted bed.
2. Characterization techniques developed for coal tar liquids.
3. Structural analysis of hydrotreated coal liquids.
4. The measurement of boiling point of coal liquid by thermo-gravimetric analysis method.

CHAPTER III

REVIEW OF THE WORK PROGRAMME

A. A brief background of the liquefaction programme

Among the known Chinese coal reserve of 700 billion tonnes, lignites and bituminous coals of high volatile and sulphur contents account for a majority of the reserved. One-third of the reserve having sulphur content higher than 2%. Alternative ultilizations of these coal resources other than power and steel making is one of the major goals of the Chinese Government in self-sufficiency in energy. Liquid fuels derived from coals with low sulphur contents for transportation, heating and industrial applications are the objective of the long term R&D programme "Techniques of Direct Coal Liquefaction". In the officially signed project document for the Phase II work of the programme (project number: CPR/83/002/A/01/37, dated: Feb. 1, 1985) several immediate objectives were identified. One of the objectives is **to develop laboratory methods for the separation of coal liquids and determination of their chemical structures and properties.**

B. Status of the analytical service

Under the liquefaction programme a comphrehensive analytical infrastructure has been implemented. Strengthening the analytical service in terms of better equipments and personnel to support the ongoing in-house liquefaction and related programs are the main goal. A few researchers, such as those to be trained in specialising field on GC-MS, has been sent abroad for the operation and maintainence training on the purchased equipments. This is only applicable in those cases where the facilities belong to higher price bracket. Undoubtedly, they are keen to pursuade for perfacting all the essential state-of-the-art analytical techniques and are seeking means to improve the analytical service to support the in-house research programmes. They also realized that all the feed-stocks, intermediates, raw products and refined products (e.g. hydrotreated coal derived liquids or distillates) have to be carefully characterized, assayed and evaluated at the various levels of analytical details. Definitely, one will observe that they already have a good start and begin to generate meaningful evaluations on the various liquefaction processes for their model candidate coals.

The following is a short list of the analytical instrumentations installed and in operation:

1. Varian (U.S.A) FT-80A high resolution nuclear magnetic resonance spectrometer for **H-1** and **C-13 NMR**. Use for the determination of aliphatic vs. aromatic hydrogen (H) and carbon (C), and the various group types of H and C, e.g. **CH** , $\mathbf{CH_2}$, $\mathbf{CH_3}$, O-$\mathbf{CH_2}$, *sp*^{2}-**CH**, etc.

2. Perkin-Elmer (U.S.A.) computerized dispersive type infrared spectrophotometer (model 580B). Use for the evaluation of **aliphatic CH** vs. the **aromatic CH** content.

3. Various sulphur analysers, proximate analyser and C,H and N ultimate analyser by LECO (U.S.A), e.g. S-32 sulphur determinator; home-make sulphur analyser based on Coulometric titration of sulphur dioxide generate from sample combustion in a high temperature tube furnance.

4. Thermal analysis (TA) system:

(a) One make in Britain, for simultaneous aquisition of thermogravimetric analysis (TGA), differential TGA (DTG), and differential thermal analysis (DTA). Use for characterization of coal, coal macerals and solid coal products.

(b) Vacuum Technics (Japan), model HP-DT/DT-2000M for high pressure DTA and differential scanning calorimetric (DSC). Use to study the thermochemistry involved with gas-solid, gas-liquid and gas-liquid--solid three phase reactions.

5. Coal calorific determinators:

(a) Standard Instrumentation Inc. (U.S.A.), model CP-500 Calorimeter recently installed.

(b) Home-made calorimeter, designed and built by the institute, model HYR-25 Oxygen Bomb Calorimeter, currently undergoing improvement to integrate new features, such as micro-processor control and data station.

6. Gas chromatographs (GC) of different makes for gas and liquid analysis; a Japanese make one is served as on-line gas analyser for the No.1 continuous process unit (CPU1); one by a Beijing GC factory in co-operation with Varian China, type: capillary GC for liquid structural analysis.

7. High performance liquid chromatograph (HPLC): one preparative HPLC unit fromWater Associate (U.S.A.) and one analytical HPLC from Shimadzu (Japan) Gradient LC System; use for hydrocarbon group-type seperation and analysis.

8. Carlo Erba (Italy) surface area and pore size analyser for coal, coal solid products and catalyst study related to the current liquefaction programme.

10. Coal petrographic analyser and accessories, e.g. Opton, model SMP-01.

11. Automatic Montana Wax Extractor model BC-I: designed, built and patented by the institution.

C. Group Discussions

1. The current liquefaction objectives

As pointed out by Mr. Dai Hewu, director of the Institute of Coal Chemistry, that liquefaction of Chinese coal require close international cooperations and UNDP inputs to make the programme a success. More importantly, is to promote strong interactions of the Chinese researchers with other international coal liquefaction groups or centres. Mr. Dai strongly pointed out the various advanced liquefaction techniques developed in U.S.A., Japan, West Germany, England, Poland and Australia all having their own merits in their own respect. More importantly they are keen to learn and to persuade all the available technologies, so that appropriate technology can be evaluated and chosen to best fit the characteristics of the Chinese coals.

They realised that the eighties being a crucial period for the preparation and maturity of the liquefaction technology, so that they can get ready for commercialization in the nineties. They viewed the training of skill personnel and the access to the know-how of the feasible liquefaction technology are the most important assets that they would possible need at this stage. In short, they would like to fulfil the following objectives:

* Select and evaluate the potential candidate coals in terms of the quaility of the coal, the reserve and transportation of raw materials.
* Technical feasibility study for the selected candidate coals in terms of the ease of liquefaction characteristics and qualility of raw and upgraded liquid products;
* To produce the most desirable fuels, in particulars the diesel fuel which the nation has an urgent need at all time;

* The raw coal derived liquids as chemical feedstocks for producing benzene, toluene, xylenes (BTX) and other key organics with good market values;
* To make use of the wastes or less desirable materials, such as the pre-asphaltene or vacuum distillate residue to produce useful products, such as active carbons and carbon fibres.

In addition, due to the national hard currency restrain they preferring to have less capital intensive smaller commercial liquefaction plants which can be financed and managed through the local infrastructure.

2. Basic scientific research related to Chinese coal liquefaction characteristics.

They realised the insufficiency of an overall evaluation of liquid products based on all the available analytical instrumentations. The problem can be understood from the fact that the majority chemists and technicians are to a great extent devoted their efforts in one or few narrow aspects of analytical methods. Creative evaluation of the coal derived products using multiple approaches and several analytical methods concurrently to provide an overall picture has yet to emerge. Undoubtedly, this is what they have to face up to the challenge.

They hope to acquire and achieve the followings:

* A Fourier Transform Infrared (FTIR) spectrophotometer for more productive and accurate aromaticity vs. aliphaticity evaluations;
* Calibration techniques and standards for gas chromatography (GC), GC-mass spectrometer (MS) and high performance liquid chromatography (HPLC);
* Basic research leading to a better understanding of the hydrogen donor solvent characteristics that dominating the coal liquefactiOon mechanisms;
* In search of the availability of cheap and effective Fe(III)-type catalyst sources for the liquefaction process, e.g. the red-mud from the bauxite processing; pyrite containing coal rejects from the preparation (washery) plants.
* Removal of the last traces of nitrogen containing components (<0.4%) from the hydrotreated coal derived liquids.

3 Other coal research activities

* The Chinese coal classification system;
* Fluidized bed combustion of coal;
* Training of M.Sc. and Ph.D. students in coal science;
* Rotary kiln study for pyrolysis and other applications;
* They also need to strengthen smaller bench scale study in parallel to the existing larger CPUs.

CHAPTER IV

RECOMMENDATIONS

There are two major areas which have been identified and require special attention and effort to get improve.

A. THE ANALYTICAL SERVICE

1. Need a general manager, with a broad background and good understanding in analytical applications development for planning, coordinating and carrying out analytical projects and problem solving. He or she will aim at establishing and promoting the value of an in-house analytical programme in supporting the coal liquefaction and other ongoing programs.

2. Modify the existing infrastructure of the analytical service by taking the following suggestions into consideration:

(a) Creating an upgrading programme for skilled analytical chemists and technicians, to encourage the individual with multi-disciplinary analytical skills and approaches; stronger interactions among the various analytical service laboratories and groups;

(b) Allocation of sufficient annual operating funding and faster means in the process of purchasing of parts, accessories, softwares and foreign service;

(c) Minimise the facility down-time, and maximize the utilisation rate;

(d) Develope an in-house programme for more interactions between operator and user, such as student and other staff member; also make room allow for limited self-service;

(e) A centralized speciality supporting workshop or service, e.g. electronic workshop for speciality equipment maintenance, trouble shootings;

(f) Training of students at M.Sc. or equivalent for selected analytical topics.

B. MORE ANALYTICAL FACILITIES

The followings outlined some of the advanced analytical facilities that might be essential for the current and future works.

1. **Fourier Transform Infra-Red (FTIR):**
   Organic functional group analysis for gas, liquid and solid samples, e.g. maceral study, interfacing with gas chromatograph (GC) for compound identifications, to improve the quality in quantitative analysis for aliphatic vs aromatic contents via computer curve fitting.

2. **High Resolution Capillary GC** equipped with selective detectors such as flame photometric detector **(FPD)** for sulphur species and thermonic specific detector **(TSD)** for organic nitrogen compounds. This would enable one to detect the harmful sulphur and nitrogen containing components in coal derived liquids on a more routine basis.

3. **Argon Inductive Coupled Plasma Spectrophotometer (ICP):**
   Essential for the analysis of trace elements associated with the raw coal derived liquids, hydrotreated liquid products, deactivation of catalyst, etc.

4. **Scanning Electron Microscope (SEM)** should equipe with X-rays energy dispersive spectrometer (EDS), capable of interfacing with an image analyser. Useful for the study of coal derived solid products, catalysts, coal macerals, mineral matters in coal, carbon materials, particle size distribution and pore structure, etc.

C. CONCLUSION REMARK

It is hoped that the above recommendations stated in Section A will provide a ba sis for a better planning of the analytical service in the future and the use of appropriate management of the service and thereby will contribute more to the overall productivity of the programme. It is also hoped that the various items suggested in Section B for more advanced analytical equipments will have to be considered seriously and justify for the liquefaction programme, definitely more funding would be required. It is also important to point out that analytical facilities be made available to other research groups within the nation working on coal science. The availability can take different routes, for example, via the format of joint research programme or research agreement or research service or conduct training programmes. The whole idea is to make the investment by the China Government and UNDP inputs even more rewarding in the coming years.

APPENDIX A

BRIEF SUMMARY OF THE CONSULTANT'S ACTIVITIES

Date		Activity
17 Nov, 1986		Leaving Vancouver, Canada for Vienna, Austria..
18 Nov		Arriving Vienna.
19 Nov		Briefing with the UNDP and UNIDO officials.
20 Nov		Leaving Vienna for Beijing, China.
21 Nov		Arriving Beijing.
22 Nov		Visit the Coal Chemisty Institute of CCMRI; discussion on the schedule and lecture content.
23 Nov (Sunday)		Private activity.
24 Nov	(a.m.)	Briefing at the Beijing's UNDP headquarter and recieving of detailed documents on the " Techniques of Direct Coal Liquefaction, Phase II".
	(p.m.)	First lecture (2.5 hours).
25 Nov	(a.m.)	Second lecture (2.5 hours).
	(p.m.)	Third lecture (2.5 hours).
26 Nov	(a.m.)	Visit the three coal liquefaction continuous process units, gasification, coking, combustion laboratories and all the major analytical facilities.
	(p.m.)	Fourth lecture (2.5 hours).
27 Nov	(a.m.)	Fifth lecture (2.5 hours).
	(p.m.)	Three selective group discussions.
28 Nov	(a.m.)	Debriefing at Beijing's UNDP headquarter.
29 Nov	(p.m.)	Dialogue with the Director, Mr. Dai Huiwu.
30 Nov (Sunday)		Private activity.
1 Dec, 1986		Leaving Beijing for Xaimen, Fujan. (lecturing at Xaimen University on Coal Science and Coal Gasification), plus private activity).
6 Dec	(a.m.)	Leaving Xaimen.
7 Dec	(a.m.)	Returning to Vancouver, Canada.

APPENDIX B

STAFF MEMBERS OF UNDP (BEIJING) AND OF CCMRI

The following short list summaries the key staff members of UNIDO (Bejing) and of the Beijing Research Institute of Coal Chemistry (CCMRI) whom I met during my duty in Beijing.

UNDP Representatives:

* Mr. Albertus W. Sissingh - Senior Industrial Development Field Adviser.
* Ms. Li Qiming - Senior Programme Officer.
* Ms. Zou Yoalan - Senior Programme Officer.

Central Coal Mining Research Institute (CCMRI):

* Mr. Yu Xiang - Deputy President, CCMRI.
* Mr. Zhang Shengtao - Deputy President, CCMRI.

Beijing Research Institute of Coal Chemistry, CCMRI:

* Mr. Dai Hewu - Director, Senior Engineer, Associate Professor.
* Mr. Yang Jinhe - Deputy Director, Director of Beijing Energy Society.
* Mr. Wu Chunlai - Associate Director, Engineer.
* Mr. Chen Peng - Director of Chinese Coking Society.

Office of International Cooperation, CCMRI:

* Ms. Pang Weizhen - Engineer.
* Mr. Yang Zhangkun - Engineer.