Coal-Tar Chemicals and Syncrude Oil Production from Low-Rank Coals Using Mild-Temperature Pyrolysis

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Ebbe R. Skov, P.E., ConvertCoal, Inc., Mission Viejo, CA, Hetagon@aol.com
Dennis C. England, Ph.D., P.E., E2 Environmental, Inc., Irvine, CA
Franklin G. Rinker, P.E., ConvertCoal, Inc., Naples, FL
Robert. J. Walty, RJW Associates, Fallbrook, CA,

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ABSTRACT A novel coal-to-liquids (CTL) process developed by ConvertCoal Inc., (CCI) for processing of low-rank coals was presented earlier at this conference (ref. 1). This paper presents a summary of the yields, composition and properties of the coal-tar-oil fractions recovered from the CCI mild-temperature pyrolysis process, prospective applications of sub-fractions, and data from catalytic hydrotreating to syncrude. In the novel CCI process, bituminous, sub-bituminous and lignite low-rank coals (LRC) are converted into coal-tar-oil that can be hydrotreated to syncrude oil, and high efficiency, low-emission clean-coal fuel for IGCC and PC-generating power boilers. The simultaneous production of clean coal and syncrude oil provides an economic basis for this new CTL process. The syncrude results from on-site catalytic hydrotreating of recovered coal-tar-oil in 15 - 20w% yields on a water-and-ash-free basis, indicating syncrude yields of 0.75 – 0.95-bbl/ton of feed-coal. ConvertCoal, Inc., has recently completed the design and patent applications for a modular mild-temperature pyrolysis plant for processing 10,000-t/d Wyoming PRB coal to produce 1150-t/d coal-tar-oil and 5000-t/d low-emission coal-char fuel matching a 500-MW power plant. The coal-tar-oil hydrogenation yields 8000-bbl/d syncrude with suitable properties for petroleum oil refining. A new “virtual oilfield resource” producing 200,000-bbl/d with predictable oil quality and defined recovery profile therefore would result from having in operation two dozen such projects corresponding to 12,000-MW generating capacity and 88-million-t/y LRC (less than 15% of annual LRC mining capacity). The capital intensiveness of the project is similar to oilfield and power projects on a barrel-per-day of oil or ton-per-day of coal basis. Current engineering studies indicate that the process can be economically attractive at current energy price levels, and it therefore could become the basis for converting the large U.S. LRC resources into equivalent oil reserves.
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1.0 INTRODUCTION

The purpose of the coal-to-liquids (CTL) process developed by ConvertCoal, Inc. (CCI) is to convert low-rank-coals [LRC] with more than 30-wt% “volatile matter” into two valuable co-products. These are a coal-tar-oil convertible by catalytic hydrotreating into syncrude oil for petroleum refining, and a low-emissions clean-coal-char fuel suitable for pulverized-coal power generation plants. The proprietary CCI SynCrude-SynCoal™ (SC2) process therefore is a “partial coal-to-liquids” (CTL) conversion process. The SC2 process is specifically designed for LRC including most bituminous and sub-bituminous coals and lignite that together comprise the most abundant coal resources in USA, PRC-China, India and the EU, representing more than two-thirds of the world’s known coal resources.

The commercial applicability of the SC2 coal conversion process is prospectively significant based on the present price for crude oil, the desire for development of domestic oil resources, and the need for improved efficiency, clean-coal fuel for the existing and future PC-generating power plants. The CCF can meet the 2010 Clean Air Initiative Regulation due to lower sulfur, nitrogen and mercury content, and also is more efficient for power generation than the feed coal. With regard to syncrude oil production, the SC2 process can deliver approximately 7500-BPSD oil for refinery feedstock based on 10,000-t/d of LRC of average composition, while also providing the low-emission clean-coal fuel (CCF) required for a 500-MW power plant. The coal-tar-oil (CTO) recovery process and conversion to syncrude oil are described below, while the SC2 mild-temperature pyrolysis (MTP) process, its development history (ref. 2) and salient aspects of the CCF product are discussed separately in another paper presented at this conference (ref. 1).

2.0 PROCESS SUMMARY

The SC2 process is based on mild-temperature pyrolysis (MTP) operating at up to 590°C (1100°F). It is applicable primarily to low-sulfur LRCs including some bituminous and most sub-bituminous coals and lignite that contain 30-wt% water and more than 32-wt% “volatile matter”. Generally a third or more of the volatile matter is converted to coal-tar-oil (CTO) producing a 11 – 14-wt% oil yield based on total feed-coal, or 16 – 20-wt% oil on a water-ash-free (WAF) basis (Figure 1, Process Block Diagram). The MTP process is preceded by coal grinding to quarter-inch and smaller particle size and a coal-drying step using recovered waste heat from the downstream process.

The entire SC2 process is based on using commercially available industrial equipment in similar service, such as petroleum coke calcining kilns. A substantial amount of process water is recovered from the drying operation and then is cleaned to meet the quality required for use as cooling water. The processed coal-char fuel (CCF) is cooled to ambient temperature, passed through a pyrite/ash removal unit and then delivered directly to the adjacent PC-generating plant. The SC2 process reduces the CCF moisture to near zero, sulfur by 50 – 75%, nitrogen by half and mercury by more than 90%. Depending on the feed-coal quality, the coal-char-fuel product can potentially meet the stringent new U.S.-EPA Clean Air Interstate Rules (CAIR-2010) for maximum 0.27-kg-SO_2 per MJ, while increasing the power boiler efficiency by 5% or more due to the removal of water by drying and pyrolysis.

The individual coal processing steps are described in a separate paper (ref. 1) with the focus here being on the oil recovery, composition and fractionation. Approximately 10 – 14-wt% of the feed-coal is converted to pyrolysis gas containing a mixture of fuel gasses (CH_4, CO, H_2) and inert gasses (CO_2, N_2, H_2O) with a fuel value between 20 – 40% of methane. The coal-tar-oil (CTO) produced in the MTP process is recovered from the pyrolysis gasses and processed into valuable products as outlined in more detail below.

3.0 PYROLYSIS OIL RECOVERY

The recovery and conversion of coal-tar oil (CTO) into useful product is the single major challenge for the economic viability of low-rank coal (LRC) pyrolysis processing. Firstly, the process design needs to overcome the yield losses of CTO resulting from the low partial pressures of the individual oil compounds due to dilution with pyrolysis gasses and heating-gas used for heat transfer in the pyrolysis reaction. And secondly, the composition of the recovered CTO is so complex that the material can find commercial application only after considerable processing. In the past these twin challenges have been the principal technology reasons preventing commercialization of CTO.

3.1 CTO COMPOSITION The pyrolysis process generates a broad spectrum of more than a thousand individual condensable materials, including aromatic and aliphatic compounds in the boiling point range 60 – 700°C, carbon number range C4 – C45, and with molecular weights from 58 to 600+ Dalton. Depending of the feedstock LRC composition, the CTO is 45 – 60-w% aromatic in nature and some fractions are rich in oxygen, sulfur and nitrogen. Table 1 provides a typical inspection of CTO, and Table 2 shows the types and weight percent of compounds found in the boiling range IBP to 662°F fraction and the toluene soluble and insoluble fractions in the 662+°F boiling range fraction.

TABLE 1
COAL-TAR OIL ANALYSIS

Analytical Method	**Parameter**	**Coal-Tar Oil**
D 287	Sp. Gr., g/ml	1.06
D 240	HHV, Btu/lb	15,555
D 97	Pour Point, °F	85
D 97	Cloud Point, °F	80
D 93	Flash Point, °F	245
D 95	Water, w%	0.97
D 473	Sediment, w%	0.19
TC	Nitrogen, w%	0.9
D 1552	Sulfur, w%	0.22
D 482	Ash, w%	0.03
Infrared	Carbon, %	77.35
Inferred	Hydrogen, %	8.05
By diff.	Oxygen, %	12.48
NMR	Hydrogen, ratio aliphatic/aromatic	7.74

Distillation [ASTM D-1160]

	Recovered Wt%	**Temperature, °F**
	5	IBP - 212
	10	414
	20	436
	30	454
	40	469
	50	500
	60	519
	70	566
	75	585
Recovered	75	~590
Residue End Point*	25	563, decomposition*
Total	100	

TABLE 2
COMPOUND TYPES IN CTO

Fraction-I, IBP – 662°F	**Wt%**
Saturated HC	
Aliphatic paraffins	4.5
Other saturated HC	2.8
Aromatics	
Monocyclic	2.2
Bicyclic	3.2
Tricyclic	0.5
Tetracyclic	13.1
Polar Compounds	
Phenol	1.5
Cresols	2.7
Other Phenols	4.1
Naphtols	1.2
Benzenediols	7.8
Subtotal	43.6
Residual Fraction-II, 662+°F	
Toluene-insoluble fraction	14.63
Toluene-soluble fraction	41.77
Total	100.00

The science of coal-tar oils is a complex art, and it is important to note that the properties and composition of mild-temperature pyrolysis CTO differs considerably from coal-tar obtained from high-temperature metallurgical coking. This is in part due to the composition of coking coals, and in part because the processing cycle in metallurgical coke ovens is much longer and reaches much higher temperatures (1000°C over 6 – 8 hours versus 600°C over 20 minutes for MTP). Higher boiling compounds therefore are volatilized and smaller reactive compounds tend to be destroyed or polymerized. The differences in CTO composition lead to different product yields and economic potentials of the various recoverable fractions.

3.2 CTO RECOVERY YIELD

The CTO yield depends on the feed-coal composition, the process design and also to some extent on the pyrolysis temperature cycle. With moderate residence times at operating temperature and a weight ratio of sweeping-heating gas to coal in the range of 1 – 3, the CTO yield curve versus temperature is relatively flat and the optimum yield is obtained in the region of 530 – 580°C. To illustrate with an example, a Wyoming coal (Buckskin mine, 8400-Btu/lb) with 30w% moisture and 32w% "volatile matter" will yield 10w% non-condensable pyrolysis gas, 13w% recoverable CTO, and 50w% of clean-coal fuel (CCF) with 13w% volatile matter and 11400-Btu/lb heating value.

Approximately one third of the LRC "volatile matter" is recovered as pyrolysis coal-tar-oil. This leaves behind the heaviest 15-w% volatile hydrocarbon compounds that are undesirable for syncrude oil processing but desirable in the coal-char for ignition and flame stability. In the MTP [pyrolysis] process about 10-w% of the coal reports to fuel gas, and 4 – 5 % of the feed-coal thermal energy is consumed in the process. The three products are treated process water that can be designed to meet power-generation plant standards, coal-tar-oil liquid convertible to syncrude oil or coal-tar chemicals, and upgraded low-emissions coal-char-fuel containing approximately 70% of the feed-coal fuel-value.

Examples showing the product yields, heat and material balances for two different coals were presented in a related paper earlier (ref. 1). In summary, project corresponding to a 500-MW capacity PC-power generation plant, using 10,000-t/d Wyoming coal, will produce 1150 t/d coal-tar-oil, 5000 t/d coal-char-fuel, 3000-t/d water and 850-t/d of a mixture of inert gas and fuel-gas. The heat balance shows the 17.7-GJ/t [16.8-mmBtu/t] feed-coal is converted into 23.6 GJ/t [22.4 mmBtu/t] coal-char-fuel, and 5w% of the feed-coal converts to fuel gas used in the process. In addition, the hydrogen production required for oil hydrotreating will use approximately 2.5% of the feed-coal.

3.3 CTO RECOVERY PROCESS

For any given feed-coal composition, the recovered CTO yield depends critically on the oil recovery process design optimization. The design challenge in part results from the multitude of individual pyrolysis compounds with miniscule partial pressures and with considerable dilution of the condensable compounds with noncondensable pyrolysis gas and sweeping-gas. The combined partial pressures of the condensable organic compounds in the exit pyrolysis gas mixture therefore may be less than 2 – 5% of the total pressure, and each individual compound may be less than one percent of that total.

Although the unit operations available to recover the CTO include low-temperature condensation, adsorption and absorption in any combination, the design optimization in operating and capital cost is far from being trivial (Figure 2, PFD-200). In addition to the optimization of the overall oil recovery yield, the proprietary CTO recovery process takes into consideration that parts of the high-boiling tar compounds are emulsifier surfactants with high viscosity at ambient temperature. Also, some of the lower molecular weight compounds tend to crystallize and form high viscosity multi-phase sludge. These product characteristics can cause operating problems such as heat exchanger surface fouling, sedimentation of high viscosity tar compounds and emulsion formation caused by high molecular weight polar compounds dispersed in low-boiling oil fractions, that need to be avoided. The CTO recovery process therefore is designed to provide fractional condensation of the pyrolysis oil and deliver 3 – 4 separate CTO fractions as indicated in Fig.-2 showing a simplified version of the process scheme.

To provide a basis for design optimization, a sample of coal-tar-oil recovered from Wyoming sub-bituminous coal (Buckskin mine) was fractionated by distillation and inspected for physical properties. Based on a process engineering simulation, the data indicates that at the actual demonstration plant operating conditions for the pyrolysis and oil recovery sections, as much as 15 - 20% of the light-end oil compounds were not recovered in the liquid phase. Primarily this was because of too low partial pressures and a low ratio of oil to inert-gas of 4.5 - 6.0 wt%. It was also found that at room temperature the material separates into three separate liquid phases.

TABLE 3 - PHYSICAL PROPERTIES OF COAL TAR OIL, EXAMPLE

FRACTION	Total	#4	#3.1	#3.2	#2	#1
Distillation yield, wt%	100	9.4	3.2	28.7	16.6	42.1
Boiling Range, ºF	185 - 1150	IBP-450	(450-650)		650-850	850+
Specific gravity, g/ml	1.081		0.938	1.049	1.049	1.09
API Gravity, 60ºF	1 - 3		19.4	3.4	3.4	~1.5
Viscosity, 122ºF, CS	280					
Pour Point, ºF	66 - 90					
Flash Point, ºF	170 - 240					
Water, wt%	1 - 2					
Sediment, coal fines, wt%	1 - 3					
Heating value, Btu/gal	140,000					
Acid number, mg KOH/g			0.6	3.2	1.3	5.1
Elemental analysis: wt%						
Carbon	79.5		82.7	78.3	83.4	83.2
Hydrogen	8.62		10.5	8.6	9.7	7.8
Oxygen [by diff.]	9.79		4.2	11.2	6.1	7.4
Nitrogen	0.54		0.22	0.49	0.35	0.47
Sulfur	0.52		0.26	0.31	0.32	0.33
Ash	nil		-	-	-	-

4.0 CTO CHEMICAL INTERMEDIATES

The individual CTO fractions recovered from the pyrolysis vapor can be hydrotreated to syncrude oil as described below, or further fractionated into chemical intermediates. The coal-tar chemical industry has a long history of extracting valuable intermediate products from coke-oven condensate. Industries using naphthalene, BTX (benzene, toluene and xylenes), phenolic compounds, cresylic acids and cresols originally relied on their feedstock from coal-tar oils. Although the petrochemical industry can now supply some of these chemical compounds more cost effectively, the market for specialty coal-tar chemical intermediates is still expanding based on coke-oven derived material.

4.1 CTO FRACTIONATION When CTO is fractionated by distillation, each fraction is found to contain a mixture of non-polar compounds including aromatic, aliphatic and cyclic hydrocarbons, and more polar compounds including substituted phenols, cresols, alcohols, their homologue sulfur compounds and amine compounds. It is therefore necessary to apply both solvent extraction and distillation to separate the product fractions with sufficient definition and purity for commercial application (Figures ref. 3 and 4).

The combination of processing steps depends on the selected product slate and desired product purity. An example of the product slate based on a combination of solvent extraction and distillation was tested in pilot plant scale equipment with CTO produced from Wyoming coal as shown in Table 4. At some capacity yet to be determined , it becomes cost effective to provide for the fractionation to be done on site. For example, based on a 10,000-t/d CCI project providing clean coal for a 500-MW power generating plant, the production of CTO would be approximately 1200-t/d and the individual products would be 10 – 40% thereof.

TABLE 4 - EXAMPLE OF PRODUCT SLATE AND SEPARATION PROCESSES

[Ref. Oil Fractionation Demonstration Test, 2001, KMPS, Houston, TX]

PRODUCT	Yield, Wt%	Application
Amino compounds	2.5	Amine resins
Phenolic group compounds	3.5	Phenolic resins
Cresol group compounds	5.5	Polymers
Gas Oil HC fraction	15.0	Motor fuel
Wax Compounds	32.5	Industrial wax
Electrode Binder Pitch	40.0	Electrode compound

To illustrate the characteristics of the various CTO fractions, several examples with numeric data are provided in the following. Although the individual coal compositions will change the yields and compositions of each fraction to some degree, these examples provide a general overview of the possibilities and opportunities offered by the CTO oil for chemical intermediates.

4.2 CTO FRACTIONS AND YIELDS

The fractionation provided as an integral part of the coal-tar-oil recovery process is motivated by the need for downstream separation into marketable fractions and the desire to decrease the cost of this separation. The following example serves to illustrate the pre-fractionation of pyrolysis effluent into four fractions, numerical examples of oil yields, the potential downstream separations into sub-fractions and their potential application as refinery syncrude oil, electrode binder pitch, feed for wax products and coal-tar chemicals. This example illustrates just one version of the process as to the number of fractions, yields, temperatures or downstream processing or disposition of the products. This multi-step recovery process results in the separation of four liquid fractions and a gas-phase. This separation is useful because these fractions are designated for different downstream processing. The oil yields are typical ranges for Western low-rank-coals.

TABLE 5 - EXAMPLE COAL-TAR-OIL FRACTIONS

Fraction		Temperature	Oil-Yield	Examples		Feedstock	Downstream
#		ºF	Range, wt%	wt%	wt%	Fraction	Processing
1	A	850+	18 - 42	18		syncrude	hydrocracking
	A-1				18	syncrude	delayed coking
	A-2			-	15	binderpitch	visbreaking
2	B	650 - 850	16 - 34	31		syncrude	hydrocracking
	B-1			-	15	waxes	extraction
	B-2			-	15	binderpitch	visbreaking
3	C	450 - 650	25 - 40	28		syncrude	hydrotreating
	C-1			-	14	waxes	extraction
	C-2				14	syncrude	hydrotreating
4	D	250 - 450	9 - 25	23			
	D-1				10	syncrude	refining, HT
	D-1			-	10	cresylics	extraction
	D-2			-	3	pyridines	extraction
Total A - D		250 - 850+	100	100	-		
4	E	135 - 250	1 - 2	-	0.5	naphtha range hydrocarbons	
	Water	135 - 212	-	-	-	-	
5	F	Non-condensable gasses	-	-	-	reports to fuel gas	

4.3 HIGH-BOILING FRACTIONS: 650+ºF and 850+ºF (FRACTIONS 1 and 2)

As a basis for evaluation, a sample of coal-tar-oil was fractionated by distillation and the 650+ºF fraction was separated by short-path wiped-film vacuum distillation into a lower boiling wax fraction [650 - 900ºF] and a residual pitch fraction [950+ºF]. Both fractions may have considerable higher value as chemical intermediates than as refinery feedstock for motor fuel. The wax and pitch fractions also can be separated by solvent extraction as is practiced for extraction of wax from coal. The wax fraction was separated into various fractions with characteristics that match market specifications. After separation, the pitch fraction can be thermally treated at 1400 - 1500ºF to convert it into higher value "electrode-binder pitch". Material not converted into specialty product can report to the syncrude pool for use as feedstock for oil refinery processing with visbreaking, delayed coking, hydrocracking or, as the most probable option, catalytic hydrotreating.

Electrode-binder pitch for electrode manufacturing is made from high-temperature coke-oven tars. However, the 650+ºF fraction of MTP coal-tar-oil can serve the same purpose after undergoing thermal cracking at 1300 - 1500ºF. Depending on the LRC feedstock quality, the MTP process temperature and residence time, and the selected coal-tar fraction, a suitable electrode-binder pitch can be produced. Samples of 650+ºF and 900+ºF fractions distilled from MTP coal-tar-oil were tested for this purpose.

The characteristics of the 600-950-F and 900+F fractions were determined from samples of pitch fractions from coal-tar-oil recovered from MTP and HTP that were prepared by distillation under vacuum and analyzed. The results are shown in Table 6. The data clearly show the differences between coke-oven coal-tar pitch and CTO from mild-temperature pyrolysis.

TABLE 6 - CHARACTERISTICS OF PITCH FRACTIONS FROM COAL TAR OIL

Coal-tar type process		High-temperature Coke-oven-pitch	Mild-temperature pyrolysis at 950 - 1100ºF	
Characteristic:		Typical Spec	Fraction 2	Fraction 1
Fraction		700+ºF	650-850ºF	850+ºF [a]
Softening point	*	88 - 121ºC	48ºC	65 - 91ºC
Sp.Gr., at 25ºC, g/ml		>1.32	1.117	1.122
Flash point, COC		-	-	254ºC
Atomic ratio, H/C		>1.75	-	1.175
Coking value	*	55 - 60%	25%	36%
Ash		0.25%	Nil	nil
Sulfur		<0.6	0.3	0.3
Distillation to 680ºF		2.5	<3.8	<1.0
Toluene insoluble, wt%	*	7.7	-	
Quinoline insoluble, wt%		8 - 15	-	-
Total soluble in CS_2		-	-	70%

[a] Pitch fraction Distillation bottoms, 250ºC, 20-mm Hg abs.
[*] Certain minimum requirements for use as "electrode binder pitch"

4.4 MID-RANGE BOILING FRACTION - 450 - 650ºF (FRACTION 3)

The following tables show a typical example of the CTO-450 – 650ºF fraction characteristics for illustration. This CTO fraction was further fractionated by distillation and the composition determined by GC. In addition to non-polar hydrocarbons in the gas-oil range, it contains valuable chemical compounds that are highly polar in nature. Depending on the feed-coal and pyrolysis operation, the weight ratio of polar compounds to non-polar hydrocarbons is in the range of 0.10 - 0.25.

TABLE 7 – COMPOSITION OF FRACTION 3 (450-650ºF)

Composition basis:	Total Coal-Tar w%	Fraction 3, w% (450 - 650ºF)
Compound Group		
Alkyl-phenolics, cresylic acids	7.1	23
Alkyl-indanols, naphthols and biphenylols	3.5	12
Alkyl-pyridines, quinolines, amine-bases	2.6	9
Alkyl-naphthalenes	0.5	2
Non-polar hydrocarbons	14.8	49
Other compounds	1.5	5
Total	30.0	100

TABLE 8 - SUB-FRACTIONS FROM 450-650ºF FRACTION

SUB-FRACTION	3-A	3-B	3-C	
Characteristic	Acids	Bases	Neutrals	Total
Fraction of total CTO, wt%	15.2	2.1	14.6	31.9
Sub-fraction of Fraction II, wt%	47.7	6.6	45.7	100.0
Analysis				
C	74.3	76.9	85.7	
H	7.5	8.2	11.2	
O	17.9	9.6	2.2	
N	0.03	4.6	0.5	
S	0.3	0.7	0.4	
Total	100	100	100	
Ratio H/C	1.57			
SpGr., g/ml	0.814			
Composition, phenol-free basis				
aromatics		-	51.0	
n-paraffins	-	-	3.8	
iso-paraffins	-	-	13.9	
naphthenes	-	-	7.4	
olefins	-	-	19.9	
others	-	-	4.0	
Total	-	-	100.0	

Ref. BDM 9/20/97

4.5 LOW-BOILING FRACTION0 206 - 480ºF The low-boiling compounds are in particular prone to escaping capture in the oil recovery process due to the dilution of the vapor phase with non-condensable pyrolysis gases. Pilot and demonstration plant data therefore will differ with each other and with analytical laboratory results as to the actual performance of the pyrolysis and oil recovery sections. As mentioned above, once the partial pressures of the individual compounds are duly considered, the discrepancies between data bases can be understood and the process design can be optimized. A sample of coal-tar-oil was further fractionated by distillation to identify the low boiling fraction from the initial boiling point [IBP] to 482ºF [bottom temperature]. The distillation range of this fraction at normal pressure was as shown in Table 9. The composition of the recovered distillate was 50/50 oil/water. As expected the oil is mostly low boiling C5 - C7 hydrocarbons that co-distill together with water at 97 - 110ºC.
The actual yield obtained of this fraction in pilot plant operation was only 1.0 wt% of the total recovered coal-tar-oil; however, in view of the plant design and the observations above, it can be concluded that the actual pyrolysis yield was considerably larger, in spite of the relatively modest “recovery yield”.

TABLE 9 - DISTILLATION OF LOW BOILING FRACTION

Distilled Volume wt% of total oil	Condensation Temperature		Bottoms Temperature	
	ºC	ºF	ºC	ºF
IBP	101	214	154	309
0.25	98	208	174	345
0.50	97	206	193	379
0.75	98	208	220	428
1.00	110	230	250	482

4.6 POLAR COMPOUND GROUP IDENTIFICATION Solvent extraction combined with distillation provides distinct fractions of functional similar, homologous groups of compounds, as shown in the following two tables. In this manner the strongly polar compounds can be separated from the non-polar material. The cresylic acid fraction containing phenols, cresols and catechol compounds was separated from the 450-650ºF fraction and the compounds were identified with GC/MS assay (Tables 10 and 11). Several samples from coal-tar-oil recovered from a plant test operation were fractionated in order to determine variations in operation and CTO composition over time at "nominal steady-state" operation. Out of more than a thousand compounds found in CTO, more than 165 individual polar compounds were identified.

TABLE 10 - CHEMICAL COMPONENT FRACTIONS OF COAL TAR OIL

Lab Run		#1	#2	#3
	Compounds	wt%	wt%	wt%
Methyldichloride soluble fraction:				
Compound group:				
Cresylic acids [phenols]	18	6.2	5.94	6.9
Catechols	24	4.7	4.69	3.5
Neutral HC oils	86	74.11	incl	74.1
N-bases	24	2.65	incl	3.5
Ether-extract fraction.	13	5.24	incl	5.3
Methyldichloride insoluble	15+	15+	incl	6.7
Other	+	nil	86.11	nil
Total	165+	100.00	100.00	100.0

TABLE 11 - COMPOSITION OF CRESYLIC ACID FRACTION OF CTO

I	**Cresylic acid fraction**: 5.9 wt% of total coal-tar oil		
	Compound:	**wt% of fraction**	**wt% of total**
	Phenol	15.0	0.88
	o-cresol	9.0	0.53
	m/p-cresol	30.5	1.83
	2,4/2.5-xylenol	7.0	0.41
	p-ethyl-phenol	8.0	0.47
	Me-Et-phenol	8.6	0.51
	Identified others	11.5	0.68
	Unidentified others	10.0	0.59
	Total	100.0	5.90
II	**Catechol fraction**: 4.67 wt% of total coal-tar oil		
	Compound:	wt% of fraction	wt% of total
	Catechol	38.4	1.79
	3-m-catechol	10.5	0.49
	4-m-catechol	30.8	1.44
	Others	20.3	0.95
	Total	100.0	4.67

5.0 CONVERSION OF CTO TO SYNCRUDE

The CTO recovered from the pyrolysis process can be converted to syncrude oil by catalytic hydrotreating (C-HT). For C-HT, the CTO characteristics of primary importance are the relatively high content of oxygen at 10 – 11-w%, high aromatic content at 60 – 70-w%, relatively low sulfur content at 0.3-w%, and the absence of asphaltenes and associated metal compounds usually encountered in residual petroleum oil. The latter is very important because it facilitates the C-HT process, reducing catalyst contamination and results in better product yield and quality than would be expected otherwise from petroleum refining C-HT.

TABLE 12 - HYDROTREATING OF CTO MIDDLE DISTILLATE

FEEDSTOCK:	**CTO**		**CTO Soln.***		**PETROLEUM GAS OIL**	
BP Range, °F	450 - 650		450 – 650		450 – 650	
Oxygen, wt%	11.7		10.5		negligible	
Sulfur, wt%	0.328		0.295		0.711	
Nitrogen, wt%	0.544		0.490		0.013	
Hydrogen, wt% by NMR	8.54		8.55		13.09	
Specific Gravity, g/ml 60°F	1.052		1.034		0.856	
API Gravity @60°F	5.2		7.1		33.4	
[*] Toluene solvent added, %	0		10		0	
EXPERIMENTAL OPERATING CONDITIONS:						
Catalyst, Ni/Mo/Al_2O_3, HT Inc.		-------------------TK-555 Catalyst---------------------------				
Operating Temperature, °F		675	675		675	675
Operating Pressure, psia		900	900		900	900
Linear Hourly Space Velocity		2	4		2	4
Hydrogen flow rate, SCF/bbl		5000	4000		3000	3000
EXPERIMENTAL RESULTS:						
Hydrogen consumption, SCF/bbl		2100	1600		468	222 - 242
Water from reaction products, wt%		8.8	7.2		-	-
Product Specific Gravity, g/ml 60°F		0.900	0.926		0.841	0.847
Product API Gravity @60°F		25.7	21.3		36.8	35.6
H in oil, wt%		11.3	10.7		13.8	13.4
S in oil, wt%		0.017	0.041		0.005	0.010
N in oil, wt%		0.168	0.357		0.005	0.010
O in oil, wt%		2.12	3.87		-	-
Phenolic O, wt%		0.15	0.27		-	-
Conversion Efficiency: HDS, %		94.6	86.8		98.6	98.6
HDN, %		68.1	31.3		61.5	23.1 - 61.5
HDO, %		79.5	62.0		-	-
CONVERSIONS:	Feed, wt%	Products, wt%		Feed	Products, wt%	
Total saturated HCs	32.3	44.0	37.7	65.7	84.0	78.7
Polyaromatics	46.6	20.7	33.8	16.1	3.1	5.3
Thiophene aromatics	5.7	1.0	1.7	7.7	0.2	0.3
Total aromatic HCs, wt%	67.7	56.0	62.3	34.3	16.0	21.3
Simulated distillation curve shift at 20%-vol, °F		115	85		25	12
At 50%-vol, °F		55	10		25	10
At 80%-vol, °F		40	20		14	7

[Ref. 3]

Table 12 provides an example of the test results from catalytic CTO hydrotreatment, albeit the CTO fraction in the example is a 230 – 345°C (450 – 650°F) midrange distillate similar to a petroleum atmospheric gas-oil with which it is compared in the table. As shown in this example, due to C-HT processing the oil product volumetric yields increase by 16.8% and 1.8% respectively based on the corresponding decreases in density. This is due to the decrease in product density as the ratio of hydrogen to carbon increases; however, simultaneously the reactions of oxygenated compounds with hydrogen results in a loss of reaction water and hence also weight and volume. Similarly there are some losses associated with the removal of sulfur as H_2S and nitrogen an NH_3.

The results from the catalytic hydrotreating (C-HT) of CTO middle distillate fraction provide important data for economic evaluation of the conversion of the other fraction of CTO presented in the foregoing to syncrude oil. Firstly, the compounds in the heavier CTO fractions are for the most part homologues of the middle distillate fraction, just with more alkylation and larger molecular weights. Therefore, although reactivity towards C-HT will vary somewhat with molecular weight, the reaction conditions and hydrogen uptake will be similar, albeit a little less as the weight percent of oxygen is inversely proportional with mol-weight. Secondly, the compounds found in the lighter fractions for the most part also are similar homologues. However, two factors also decrease and mitigate the hydrogen uptake of the lighter fractions containing relatively higher oxygen and nitrogen by weight. Firstly, the yield of the CTO 450°F-minus fraction is small to start with; and secondly, more than two thirds of this fraction is more valuable as feedstock for chemical intermediates, and can more readily be extracted from the whole CTO. It is therefore reasonable, while more data is developed to simulate the C-HT reaction for the whole CTO fraction (minus the valuable cresylic acids fraction) based on the available data presented here.

The syncrude oil resulting from CTO C-HT processing is characterized by practically not having any "residual oil" compared with the 1100+°F asphaltene-maltene fraction in petroleum crude oil. This is due its origin essentially as a distillate from the mild-temperature pyrolysis process. Therefore it contains no compounds with molecular weight above 650 Dalton, as compared to asphaltenes at 2500 Dalton and up. Also, unlike crude petroleum oil there are no metal (V, Ni, Fe, Mo) contaminants present in the CTO that could adversely affect the C-HT catalyst. Even so, for several reasons including C-HT unit capacity and cost, it still may be most cost effective to select the C-HT process from among slurry catalyst processes.

6.0 HYDROTREATING PROCESS AND HYDROGEN SUPPLY

The catalytic hydrotreating process for conversion of CTO to syncrude can be either a fixed-bed or slurry type design. There are several commercial processes of both types available and both types have merit for this application since CTO contains no metals or asphaltene fraction.

6.1 HYDROTREATING PROCESSES Advantages for the fixed-bed catalytic process include the simplicity of design and operability, and the recent significant advancements of HDS catalyst activity and operating life resulting from the ultra-low-sulfur diesel HT process demands. Potential disadvantage may be the cost of catalyst, downtime due to catalyst change-out and limited catalyst life as was found in 1997 with the earlier generation of catalyst. Points in favor of slurry-type catalyst HT-processing are the cost of catalyst, continuous catalyst substitution, and the relative simplicity of design. Ultimately the choice of process will be based on the combined economics of product quality and yield, operating cost relating to operating pressure and temperature, catalyst cost and capital cost for the selected capacity.

6.2 HYDROGEN SUPPLY The hydrogen supply upstream of the C-HT process is obtained from gasification of CCF to syngas (i.e., H_2 + CO), followed by conversion of CO via high-temperature and low-temperature shift reactions to hydrogen. Purification to 85 – 95% H_2 is done by CO_2-removal and H_2S removal with amine-absorption (and H_2S conversion to disposal sulfur via known refinery processes), which is followed by compression to the operating pressure. All these processes are so well known and in industrial operation in so many plants that little needs to be added here.

6.3 CTO COKING OPTIONS Considerable work has been done to determine the results of CTO conversion to refinery feedstock via conventional high-temperature processing such as visbreaking, coking and catalytic cracking. Based on the CTO composition before C-HT, the products are similar to the performance of the equivalent petroleum fractions, with the caveat that the reactive components containing oxygen, sulfur, nitrogen and olefins predictably produce free radicals, side reactions, cracking gasses and coke formation in proportion to their concentration. This may not become an issue when the economics are favorable, and when the operation is properly adjusted for the quality of the feedstock.

The alternative is to first do the C-HT processing step, albeit at the cost associated with the hydrogen supply and capital charges; then process the higher boiling fractions in the same fashion as is done with the petroleum gas-oil fractions. Again here, the choices depend on the project specific economic evaluation.

6.4 COKING TEST RESULTS To illustrate the CTO conversion, the following table shows an example of coking performed at several different temperatures in a petroleum testing lab facility using two different distillation fractions from untreated CTO. The CTO sample was fractionated by vacuum distillation into a 650-900ºF fraction and a 900+ºF fraction, and each fraction was subjected to delayed coke processing at two different conditions, as shown below. The recovery yield of distillates is 52 - 61wt%, coke 32 - 42 wt% and fuel gas 3.5 - 4.3 wt%. It can be appreciated that results after C-HT of the CTO would be considerably more favorable towards better gas-oil yields and less coke production.

TABLE 13 - RESULTS OF COKING TESTS

COKING TEST	**A**	**B**	**C**	**D**
CTO-fraction No.	2	2	1	1
Boiling Point Range	(650 - 900ºF)		(900+ºF)	
CTO Yield, avg. wt%	17	17	42	42
Test condition, (ambient pressure)				
Temperature, avg., ºC	505	535	515	540
ºF	941	993	959	1004
Mass balance:	--------------------wt%-------------------			
Gas, noncondensable	3.5	4.2	3.7	4.3
Distillate fractions:				
Gasoline	6.6	7.8	7.2	7.3
Diesel range	13.1	13.3	13.3	13.8
Heavy gas-oil	43.8	40.6	31.6	31.3
Sub-total distillates	63.5	61.7	52.1	52.4
Coke	31.9	31.8	42.3	41.4
Total recovery	98.9	97.8	98.1	98.1

7.0 PROCESS MATURITY AND ECONOMIC PERSPECTIVE

The process is developmental since no commercial plants in operation, yet the individual process steps and equipment elements of the process have been tested in various configurations. The issues of process maturity and risks were presented in the previous paper (ref. 1). With regard to process economics, the estimated operating costs and return on capital look very favorable at the present. Clearly, the largest factors affecting the return on capital are in order of importance the price of syncrude and/or coal-tar-oil chemicals, the capital cost and related capital charges, the plant capacity, and finally the cost of coal feedstock. Examples of economic evaluations were presented previously (ref. 1).

As indicated, the conversion of CTO to syncrude opens the door for development of LRC already in use as power generating fuel as a domestic crude oil resource. The byproduct clean-coal fuel represents 66 – 72% of the feed-coal heating value, while the CTO accounts for just about 15%, albeit with much higher added value. Conceptually the abundant LRC resources available in the U.S. therefore could be viewed as a giant oilfield, yielding approximately 0.75 – 0.85-bbl-oil per ton LRC. For example, a 10,000-t/d coal associated with a 500-MW power plant, would produce 8000-bbl/d, and two dozen such plants would comprise a large virtual oilfield producing 200,000-bbl/d. This theme also was expanded on in the referenced previous paper (ref. 1), including the availability of LRC, synergistic interaction between the PC-generating plant and CCI project, and important benefits from increased fuel efficiency for IGCC and PC-generating plants, etc..

8.0 CONCLUSIONS

We conclude that the SC2 process developed by CCI for converting LRC into clean coal and syncrude oil is technically feasible, and that it can make a meaningful contribution to the domestic oil supply, while also assisting PC-power generating stations in reaching their “2010 CAIR emissions goals”. The coproduction of coal-tar-oil for conversion into syncrude suitable for petroleum refining presents an important opportunity to expand the domestic oil supply based on Western LRC resources. The SC2 mild pyrolysis process for LRC is technically feasible based on previous demonstration test operations and commercially available equipment in similar industrial use. The status of the technology remains developmental until the first commercial project is in operation; however, scale-up to commercial capacity does not seem to present any unusual or major engineering challenges. The prospective economic profile of the SC2 process appears sufficiently attractive to provide strong incentive for commercial development.

REFERENCES

1 E. R. Skov, D. C. England, F. G. Rinker and R. J. Walty, “Syncrude and Syncoal Production by Mild-Temperature Pyrolysis Processing of Low-Rank Coals”, AIChE Spring National Meeting, Houston, TX, 2007.

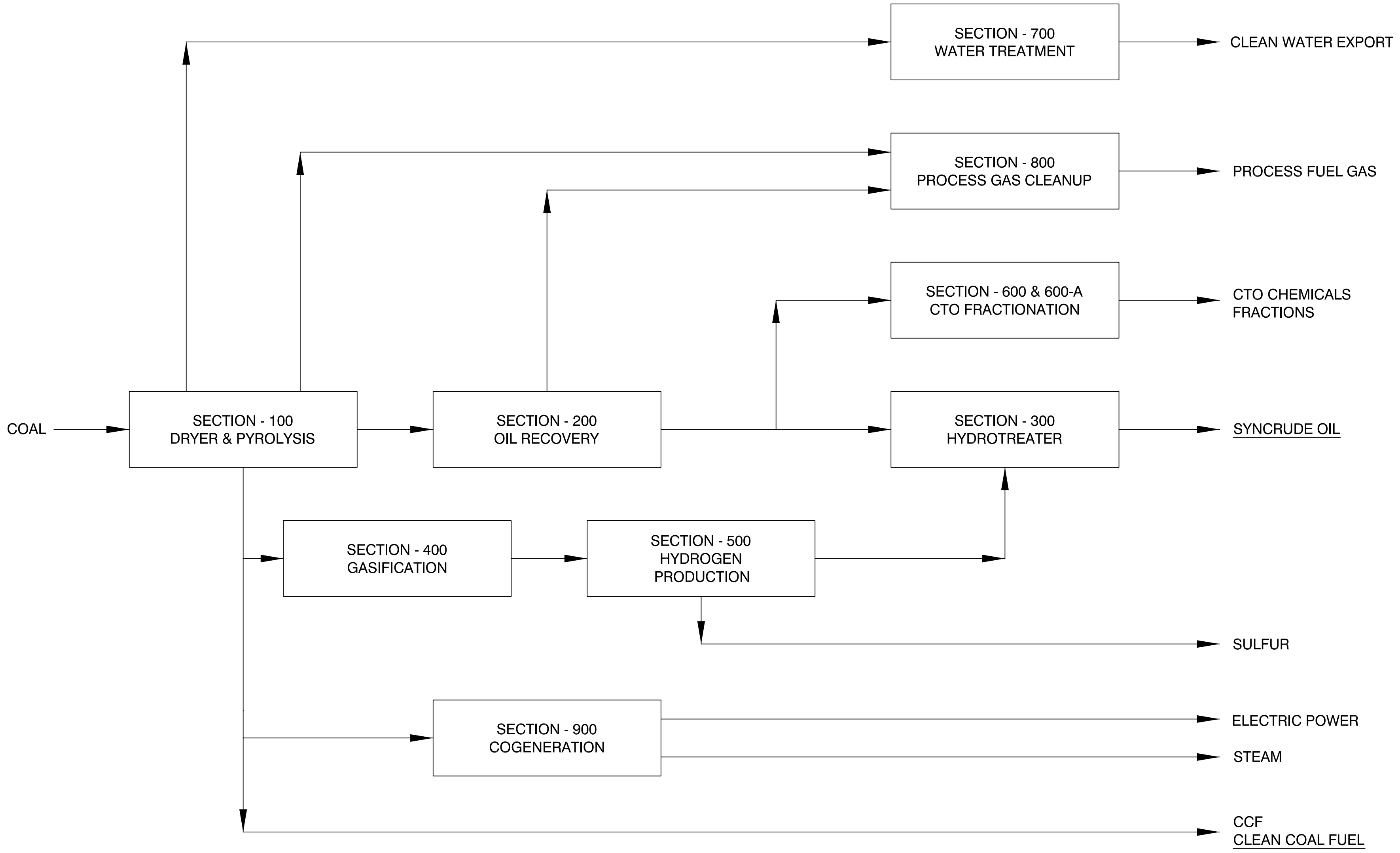
2 ENCOAL Project Final Report DOE/MC/27339-5798, US DOE Sept 1997; see also ref. 1 for additional technology developments.

3 BDM Pet. Techn., Phillips Catalyst Lab., ENCOAL Phase-1 Final Report, 9/10/97, Hydrotreating, Phillips Petroleum Lab., using HTAS TK-555 at 650°F, 900-psia, LHSV 2 and 4, with hydrogen consumption 2100 and 1600-SCFB respectively.

FIGURES ATTACHED

Process flow schematics

1	Process Overview Block Diagram
2	PFD-100, Coal Drying & Pyrolysis
3	PFD-200, CTO Recovery
4	PFD-300, Hydrotreater
5	PDF-600, CTO Fractionation
6	PFD-600-A, CTO Fractionation



ConvertCoal, Inc.

SYNCRUDE-SYNCOAL
PROCESS SUMMARY

Revision Date - 03/09/2007

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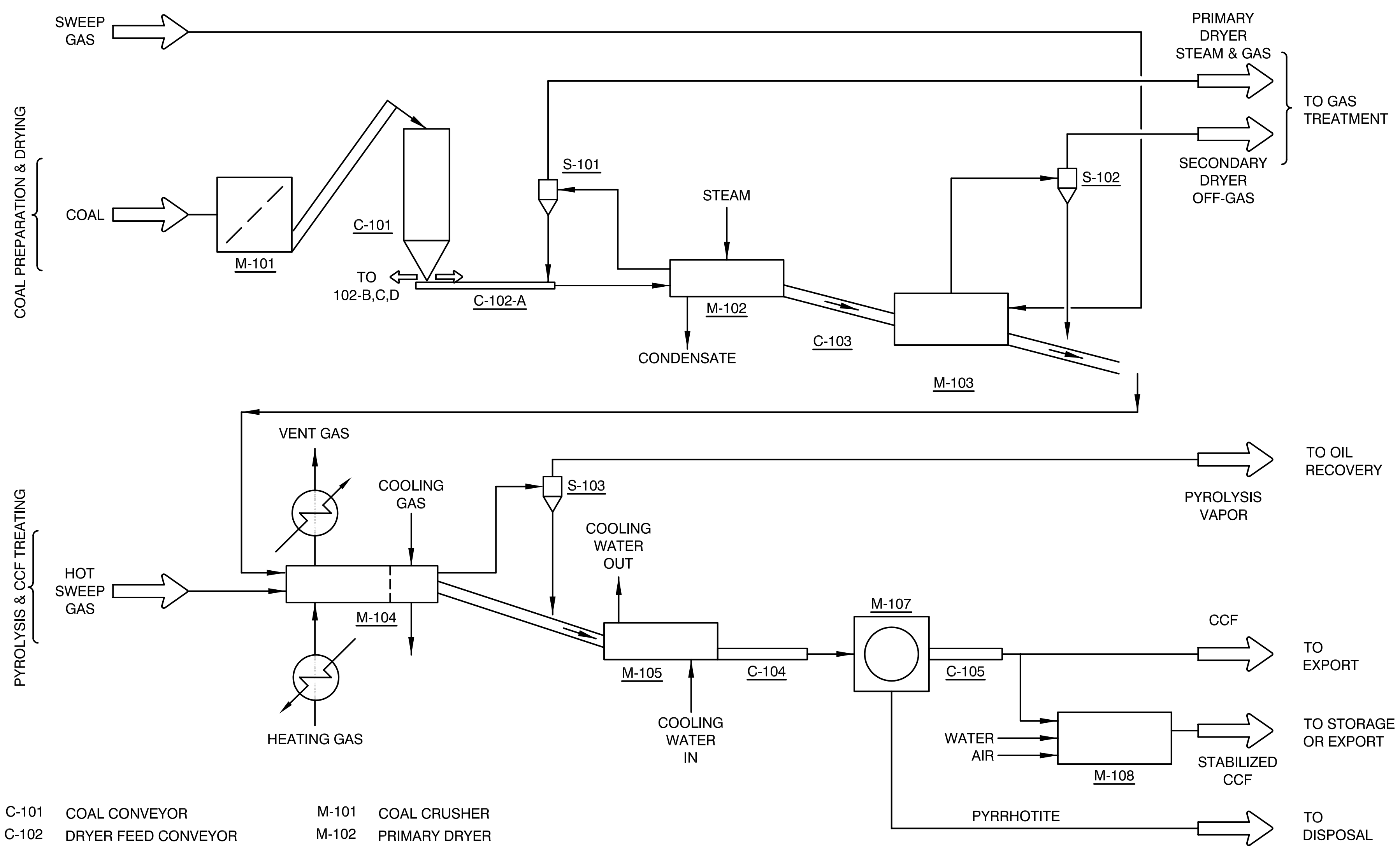

C-101	COAL CONVEYOR	M-101	COAL CRUSHER
C-102	DRYER FEED CONVEYOR	M-102	PRIMARY DRYER
C-103	DRY COAL FEED CONVEYOR	M-103	SECONDARY DRYER
C-104	COOL CCF CONVEYOR	M-104	PYROLYZER
		M-105	CCF COOLER
S-101	COAL-FINES SEPARATOR NO. 1	M-106	CCF CRUSHER
S-102	COAL-FINES SEPARATOR NO. 2	M-107	PYRRHOTITE SEPARATOR
S-103	COAL-FINES SEPARATOR NO. 3	M-108	CCF STABILIZER
Y-101	COAL SILO		

ConvertCoal, Inc.

PROCESS FLOW DIAGRAM 100

COAL DRYING & PYROLYSIS

Revision Date - 03/12/2007

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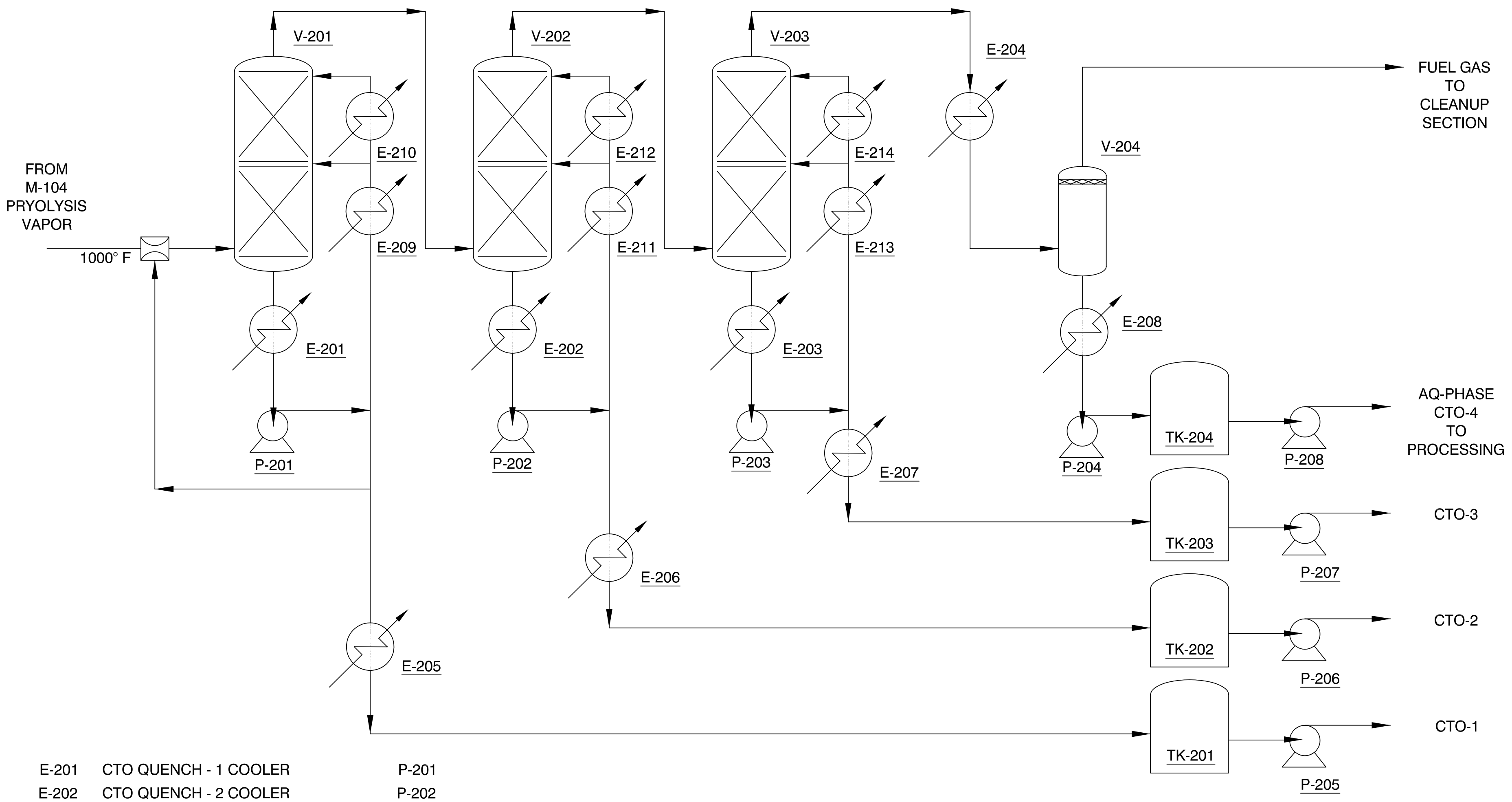

E-201	CTO QUENCH - 1 COOLER	P-201	
E-202	CTO QUENCH - 2 COOLER	P-202	
E-203	CTO QUENCH - 3 COOLER	P-203	
E-204	WATER CONDENSER	P-204	
E-205	CTO - 1 PRODUCT COOLER	P-205	
E-206	CTO - 2 PRODUCT COOLER	P-206	
E-207	CTO - 3 PRODUCT COOLER	P-207	
E-208	CTO - 4 PRODUCT COOLER	P-208	
E-209	Q-1 TRIM COOLER - 1		
E-210	Q-1 TRIM COOLER - 2	V-201	VAPOR QUENCH - 1
E-211	Q-2 TRIM COOLER - 1	V-202	VAPOR QUENCH - 2
E-212	Q-2 TRIM COOLER - 2	V-203	VAPOR QUENCH - 3
E-213	Q-3 TRIM COOLER - 1	V-204	VAPOR QUENCH - 4
E-214	Q-3 TRIM COOLER - 2		

ConvertCoal, Inc.

PROCESS FLOW DIAGRAM 200

CTO RECOVERY

Revision Date - 03/09/2007

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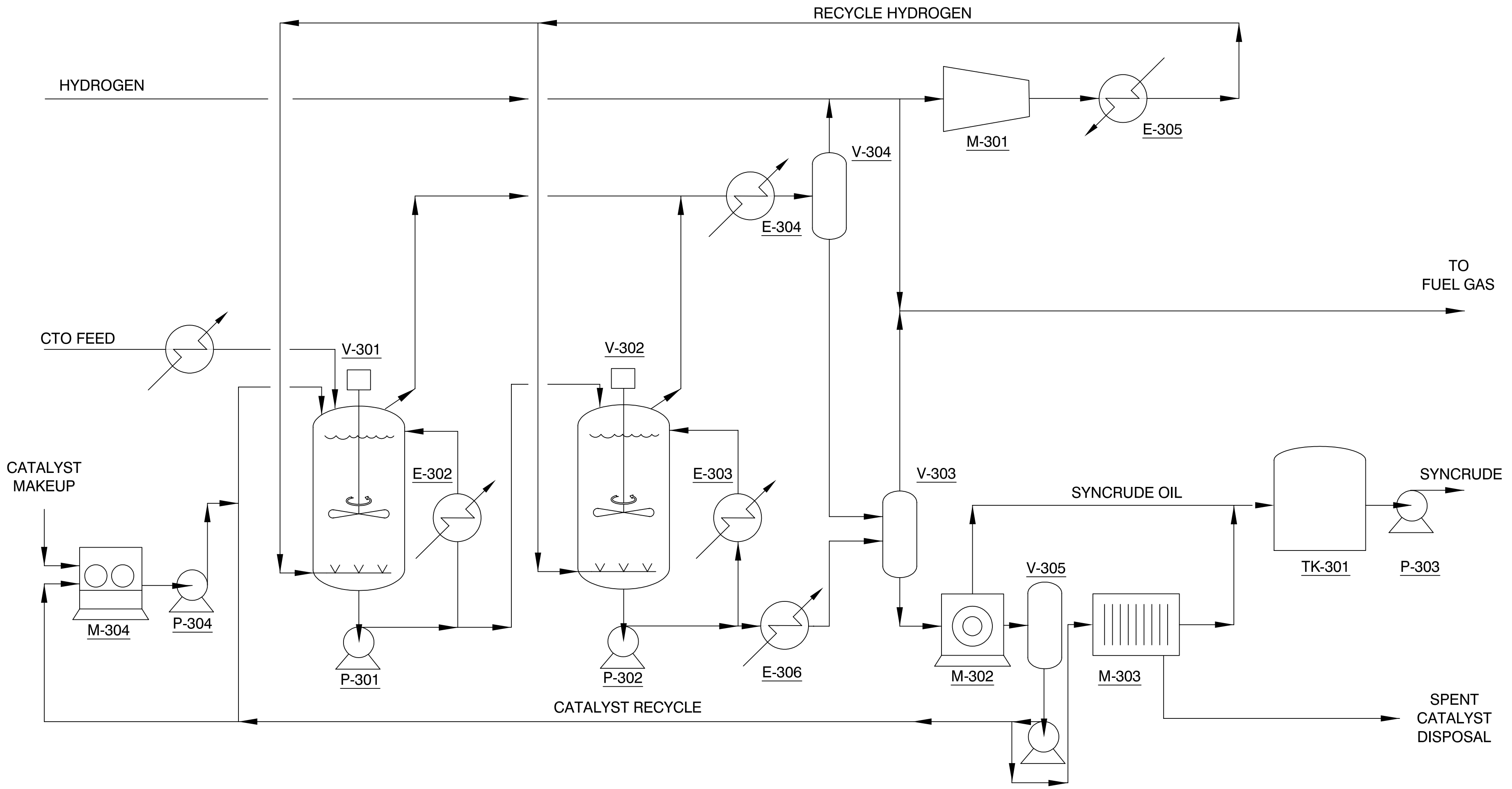

V-301	HOT-SLURRY REACTOR - 1
V-302	HOT-SLURRY REACTOR - 2
V-303	DEGASSING VESSEL
V-304	COMPRESSOR KNOCK OUT DRUM
V-305	CENTRIFUGE RECEIVER
M-301	HYDROGEN RECYCLE COMPRESSOR
M-302	CATALYST RECOVERY CENTRIFUGE
M-303	CATALYST FILTER
M-304	MAKE-UP CATALYST MIXER
TK-301	SYNCRUDE OIL TANK

E-301	HOT-FEED HEATER
E-302	HOT REACTOR-1 COOLER
E-303	HOT REACTOR-2 COOLER
E-304	RECYCLE HYDROGEN COOLER
E-305	RECYCLE HYDROGEN HEATER
E-306	SYNCRUDE OIL COOLER
P-301	HOT-REACTOR-1 RECYCLE PUMP
P-302	HOT-REACTOR-2 RECYCLE PUMP
P-303	SYNCRUDE PUMP
P-304	MAKE-UP CATALYST PUMP

ConvertCoal, Inc.
PROCESS FLOW DIAGRAM 300
HYDROTREATING OF CTO
SLURRY PROCESS
Revision Date - 03/09/2007

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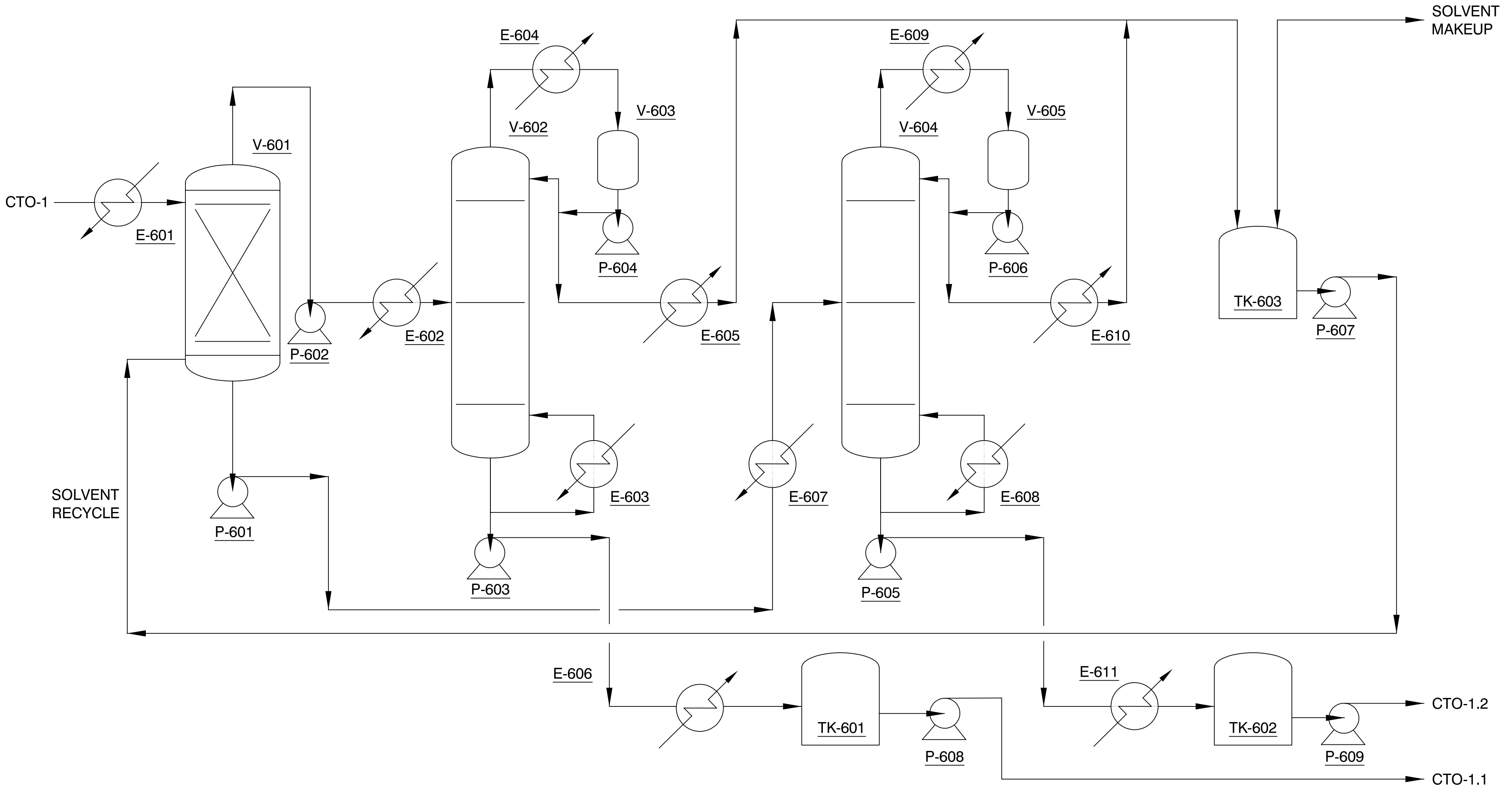

E-601	EXTRACTION COLUMN FEED HEATER	P-601	PUMP
E-602	LIQUID-PHASE HEATER	P-602	PUMP
E-603	L-P COLUMN REBOILER	P-603	PUMP
E-604	L-P COLUMN CONDENSER	P-604	PUMP
E-605	L-P COLUMN OVERHEAD COOLER	P-605	PUMP
E-606	L-P COLUMN BTM PRODUCT COOLER	P-606	PUMP
E-607	HEAVY-PHASE HEATER	P-607	PUMP
E-608	H-P COLUMN REBOILER	P-608	PUMP
E-609	H-P COLUMN CONDENSER	P-609	PUMP
E-610	H-P COLUMN OVERHEAD COOLER		
E-611	H-P COLUMN BTM PRODUCT COOLER		

V-601	SOLVENT EXTRACTION COLUMN
V-602	LIGHT-PHASE DISTILLATION COLUMN
V-603	SOLVENT RECEIVER - 1
V-604	HEAVY-PHASE DISTILLATION COLUMN
V-605	SOLVENT RECEIVER - 2
TK-601	CT0-1.1 PRODUCT
TK-602	CTO-1.2 PRODUCT
TK-603	SOLVENT TANK

ConvertCoal, Inc.

PROCESS FLOW DIAGRAM 600

CTO FRACTIONATION-REFINING
SOLVENT EXTRACTION

Revision Date - 03/09/2007