Thermochemical and Catalytic Upgrading

in a Fuel Context:

Peat, Biomass and Alkenes

Christina Hörnell

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Royal Institute of Technology
Department of Chemical Engineering and Technology
Chemical Technology

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SAMMANFATTNING

Denna avhandling avser metoder för ökad användning av alternativa bränslen. Heterogen oligomerisering av alkener för tillverkning av huvudsakligen bränslen och smörjoljor behandlas också.

I Sverige har energieffektiviteten ökat och beroendet av importerad råolja minskat betydligt sedan 70-talet men det finns fortfarande behov av ökad användning av alternativa bränslen. Väsentliga egenskaper hos råmaterialen av intresse för denna avhandling, biomassa och torv, beskrivs, liksom de huvudsakliga förloppen vid termokemisk omvandling. Utvecklingen av teknologierna för förvätskning och förgasning beskrivs.

Artikel I redogör för huvuddelen av det arbete som utfördes inom 'Olja ur torv'-projektet vid KTH. I artikel II jämförs upplösningen i tetralin av flera olika råmaterial. Råmaterialens reaktivitet befanns vara biomassa > torv > kol. Artikel III handlar om upplösning av torkad torv i simulerade recirkulerande lösningsmedel. Upplösningsgraden var beroende av lösningsmedlets aromaticitet och halt vätedonerande komponent.

Tjäror bildas oundvikligen då biomassa förgasas. Dolomit är en billig och väldokumenterad krackningskatalysator för dessa tjäror, då tillräcklig temperatur och uppehållstid föreligger återstår nästan enbart bensen och naftalen efter krackningen. Artikel IV redovisar en studie av hur tjärnedbrytningen påverkas av att kisel tillsätts en dolomitbädd.

Avhandlingen behandlar också heterogen oligomerisering av alkener. Artikel V är en genomgång av publikationer och patent som erhållits inom området heterogen alkenoligomerisering, utvärderade med avseende på använda katalysatorsystem, betingelser och produktselektivitet.

Nyckelord: torv, biomassa, förvätskning, tetralin, förgasning, pyrolys, tjärkrackning, dolomit, kisel, heterogen oligomerisering, alkener.

ABSTRACT

The thesis concerns aspects of methods for increased use of alternative fuels. Heterogeneous oligomerization of alkenes to produce mainly fuels and lubricants is also discussed.

In Sweden, efficiency in energy use has increased and the dependence on imported crude oil and oil products has decreased considerably since the 70's but there is still a need for increased use of alternative fuels. Essential characteristics of the raw materials of interest for this thesis, biomass and peat, are described as are the main reactions in thermochemical conversion. The development of the technologies for liquefaction and gasification are presented.

Paper I describes most of the work performed within the 'Oil from Peat' project at KTH. The dissolution of various raw materials in tetralin is compared in Paper II. The reactivity of the raw materials was found to be biomass > peat > coal. Paper III concerns dissolution of dried peat in simulated recycle solvents. The degree of dissolution was found to depend on solvent aromaticity and content of hydrogen-donor

Tars are inevitably formed when biomass is gasified. Dolomite is an inexpensive and well-documented cracking catalyst for these tars, when sufficient temperature and residence time are applied almost only benzene and naphthalene remain after cracking. Paper IV reports a study of the effects on tar decomposition of adding silica to a dolomite bed.

The thesis also treats heterogeneous oligomerization of alkenes. Paper V is a review of publications and patents obtained in the field of heterogeneous alkene oligomerization, evaluated in terms of catalytic systems used, reaction conditions and product selectivity.

Keywords: peat, biomass, liquefaction, tetralin, gasification, pyrolysis, tar-cracking, dolomite, silica, heterogeneous oligomerization, alkenes.

The work presented in this thesis is based on the following papers, referred to by their Roman numerals. The papers are appended at the end of the thesis.

I   Björnbom, P., Karlsson, O., Hörnell, C., Björnbom, E. and Pirjamali, M. Swedish Oil from Peat Project, *International Peat Journal*, 1987 (2), 137-162.

II   Hörnell, C., Björnbom, P., Björnbom, E., Bergström, A., Karlsson, G., Karlsson, O., Olsson, B., Solantausta, Y. and Åhgren, B. Dissolution of Peat and Wood in Tetralin Compared with Coal, in *Fundamentals of Thermochemical Biomass Conversion*, Eds. R.P. Overend, T.A. Milne and L.K. Mudge, Elsevier Applied Science Publishers, Barking, Essex, 1985, pp. 827-838.

III   Hörnell, C. and Björnbom, P. Dissolution of peat in simulated recycle solvents, *Fuel*, 1989 (16), 491-497.

IV   Myrén, C., Hörnell, C., Björnbom, E. and Sjöström, K. Catalytic tar decomposition of biomass pyrolysis gas with a combination of dolomite and silica, submitted to *Biomass & Bioenergy*.

V   Sanati, M., Hörnell, C. and Järås, S. The Oligomerization of Alkenes by Heterogeneous Catalysts, *Specialist Periodical Reports, Catalysis*, Vol. 14, Ed. J.J. Spivey, The Royal Society of Chemistry, Cambridge, 1999, pp. 236-287.

To my beloved nieces, Andrea and Mariana

CONTENTS

1 INTRODUCTION

The present thesis discusses some aspects of methods of 'alternative' fuel production: liquefaction of peat and gasification of biomass. Heterogeneous oligomerization of alkenes, to obtain mainly fuels and lubricants, is also reviewed.

After the first oil crisis in the 70's, projects for the study of liquefaction and gasification of peat and biomass were begun at the former Department of Chemical Technology, KTH. The idea was to utilize domestic fuels more and in other ways than by simply combusting them, in order to become less dependent on imports of mainly liquid fuels [1, 2].

Paper I is a summary of the work performed within the 'Oil from Peat' project at KTH. Papers II and III treat dissolution of various raw materials in tetralin and dissolution of peat in simulated recycle solvents, respectively.

Paper IV presents the results of an investigation on cracking of tars from biomass pyrolysis using dolomite, silica and combinations of the two.

Paper V is a review of alkene oligomerization by heterogeneous catalysis. Ethylene and propene, as well as butene and higher olefins can be heterogeneously oligomerized to yield liquid fuels and lubricants. Related publications and patents up to mid-1998 have been evaluated in terms of catalytic systems used, reaction conditions and product selectivity.

1.1 The importance of alternative energy sources

It is common knowledge that the world energy situation is untenable. We are all aware that we, *i.e.* mainly the inhabitants of the Western industrialized countries, are not only depleting finite fossil resources, we are also polluting the whole planet, its waters and its atmosphere as well as most probably changing its climate while doing so.

There is a vast accumulation of data to prove this. Depending on the approach, different statistics may be chosen. The Swedish energy situation in the 70's was the basis for the projects in which most of the work of this thesis was performed. The present Swedish energy situation is not substandard in comparison with that of other countries, but it is not acceptable in the long run. Some data to validate this follow.

The signatories of the Kyoto protocol have promised to lower their countries' emissions of greenhouse gases. Sweden is among the signatories. The recent Hague conference did not succeed in devising ways of obliging implementation of the promises made. In accordance with the Kyoto protocol, the European Union has undertaken to decrease CO_2 emissions by 8 % by 2008-2012, based on 1990 emissions. Within this framework, Sweden nevertheless has the right to increase

emissions by 4 %, due to the phasing out of nuclear power. These 4 % have already been exceeded [3].

Efficiency in energy use has increased and the dependence on imported crude oil and oil products has decreased considerably since the 70's. Still, it is a country where 50 % of the energy supplies were covered by fossil fuels in 1998. The remainder came from renewables (19 %), hydroelectric power (16 %) and nuclear power (15 %)[*] [4].

Sweden performs best among the EU countries as to emissions of CO_2 per GNP (Gross national product). In the EU, only Portugal emits less CO_2 per inhabitant [4]. The corresponding figures for France are very close to those for Sweden. Also Switzerland has nearly identical data. The three countries all rely heavily on hydroelectric and/or nuclear power.

Peat is not considered to be a renewable fuel in Sweden, though it acts as a medium-term CO_2 sink. About 350 000 hectares may be commercially exploitable [5], while total peatland area is about 4.5 Mha [6]. Annual long-term growth of undrained peatlands is reported to be in the order of 0.1-0.2 g carbon per square meter and year [7]. This corresponds to a total C fixation of 0.45-0.89 Mton per year. Peat utilization as a fuel in combustion, mainly for district heating, has increased considerably; in 1998 it amounted to 3.1 TWh [4], which very roughly corresponds to 0.27-0.32 Mton C.

The maximum harvestable amount, ecologically and technically, of biomass for other purposes than timber for construction, furniture and pulp, *etc.*, from Swedish forests is at present in the order of 19 Mton dry substance (including needles) per year [8]. This corresponds to about 10 Mton C.

The CO_2 emitted by transportation was about 29 Mton in 1997, 46 % of the CO_2 emitted from fossil fuels [4]. The transportation emissions thus corresponded to 7.8 Mton C that year.

Much of the remaining CO_2 emissions are neutral. They correspond to the industrial burning of black liquor, other by-products from pulp production and different types of wood remains [4]. District and domestic heating using biofuels and peat is also included. The forests grow by more than is practical to harvest, but they also decay aerobically, releasing CO_2. Of the total Swedish land area, 56 % corresponds to forests, another 11 % consists of mires while the arable land only corresponds to 7 % [6].

In UN statistic diagrams [9], modern biofuels, nuclear and renewable resources such as hydropower, solar power, and wind power are grouped together. However, the two nuclear accidents during the last twenty-five years, together with popular concern about long-term storage of radioactive wastes, has caused nuclear energy

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[*]   Figures calculated using the Swedish method. Using the UN/ECE method the figures would be 39 % fossil fuels, 15 % renewables, 12 % hydroelectric power and 35 % nuclear.

not to be seen as a sustainable alternative source of energy, but more as a traditional energy source in parallel with the fossil fuels [10].

In sum, the Swedish energy situation at present is decent in comparison with the situation in the rest of the industrialized countries but the data indicate that the situation was far from that of sustainable development, even before nuclear phasing out began. The need for greater utilization of alternative energy sources seems evident.

1.2 Heterogeneous alkene oligomerization

Almost 74 % of the most important industrial chemicals are produced from five basic chemicals: ethylene, propene, benzene, toluene and xylene. These can all be produced from biomass [11]. Of course, they can also be produced from peat.

Of the above chemicals, ethylene and propene, as well as butene and higher olefins can be heterogeneously oligomerized to yield liquid fuels and lubricants [12].

Development in zeolite catalysis led to the MOGD (Mobil Olefin to Gasoline and Distillate) process in which lower olefins from natural gas are converted into gasoline or distillate. There is also interest in increasing conventional refinery yields, by converting the light gases associated with the crude oil or those produced in the refinery into higher molecular weight hydrocarbons [13].

1.3 Structure of the work

Both liquefaction and gasification can be said to be continuations of the initial pyrolysis reactions of any thermochemical treatment of a combustible raw material. The three processes, using several input materials, are treated in the present thesis. This, and the 'coal heritage' in the studies of the processes have sometimes made boundaries between headings problematic. I have tried to resolve the difficulties by structuring the material as shortly presented in the following.

The compositions and essential characteristics of the raw materials of most interest for the work, peat and biomass, are first described. Biomass, in reality mainly wood, is described before peat since peat is the product of partially anaerobic decay of biomass.

The main reactions occurring during pyrolysis, liquefaction and gasification are then described. Development of other processes relevant for peat liquefaction, the subject of Papers I-III, is then reviewed, *i.e.* liquefaction of coal and biomass. Also flash pyrolysis processes are described. The next heading is peat liquefaction. Most of the work performed in this field has actually been conducted at KTH, the background and some of the results obtained within the 'Oil from Peat' project are treated here.

Biomass gasification, not the subject but the rationale of Paper IV, is thereafter described. The near-commercialization status of the technology makes for its rather broad account.

The papers are then summarized. Paper V, concerning heterogeneous oligomerization of alkenes, is more self-contained than the others since a rather long section on theory is included. This review is also considerably longer than the other papers, justifying the many subtitles in the summary.

2 RAW MATERIALS

A very general definition of coal is that it is 'a combustible solid, usually stratified, which originated from the accumulation, burial and compaction of partially decomposed vegetation in previous geologic ages' [14]. This definition elegantly evades all specifications as to composition and chemical and physical characteristics. Still, it makes clear the kinship between between biomass, peat and coal explaining why the three raw materials may be studied simultaneously.

Peat and biomass are the raw materials of greatest interest for the work performed. Raw material characteristics are decisive for the results obtained in thermochemical processing. Biomass, peat and their composition are therefore described, including how their properties may vary.

2.1 Biomass

Examples of biomass which may be used as raw materials in different conversion processes are forest and agricultural residues (thinnings, bark, straw, *etc.*), short rotation crops (for example poplar, *Miscanthus* and *Salix*) and wastes from agricultural and forest products processing (bagasse, rice husks, nutshells, corn cobs, planer shavings, sawdust, *etc.*). These are all quite different to the naked eye, but measurements indicate that the ultimate analyses of the dry, ash-free substances of different kinds of biomass are very much alike, as can be seen in Table 1 [15].

The fuels may not be distinguished statistically by their carbon, hydrogen or oxygen contents. It is only the nitrogen content which is significantly higher in the agrofuels. Nitrogen in living organic tissues is mainly to be found in proteins. The protein content of softwood stems is usually 0.2-0.8 %, the lowest being in heartwood. In needles and leaves, much higher protein content can be observed (7-8 %) [16].

2.1.1 Biomass composition

The principal organic constituents of biomass are cellulose, hemicellulose and lignin [17]. In many species there are also so-called extractives deposited in the cell walls. The proportions of these constituents in wood are (in percent of dry biomass): cellulose 40-45 % (about the same in softwoods and hardwoods), lignin 25-35 % in softwoods and 17-25% in hardwoods, hemicelluloses 20% in softwoods and 15-35 % in hardwoods, while the amount of extractives varies from 1 to more than 10 %.

Cellulose forms the structural framework of plant cell walls. It is composed of glucose molecules ($C_6H_{12}O_6$) linked together in long chains. The linkage of any two glucose molecules is accompanied by the elimination of one molecule of water, thus the empirical formula for cellulose is ($C_6H_{10}O_5$)$_n$ where n is the degree of polymerisation. Cellulose is a linear polymer and has a strong tendency to form

Table 1 Mean ultimate analyses, including standard deviations, of some ash-free biofuels [15]

	C	H	N	O
Wood fuels	52.4±3.9	6.1±0.5	0.32±0.30	41.8±3.9
Agricultural fuels	50.0±0.8	6.2±0.1	0.94±0.38	42.8±0.9
European agrofuels	49.4±0.5	6.1±0.1	0.58±0.28	43.7±0.5

intra- and intermolecular hydrogen bonds. The average degree of polymerisation (DP) is 9000 to 12000 glucose units [18].

The covalent bonding within and between glucose units results in a straight and stiff molecule with very high tensile strength. Lateral bonding of the cellulose molecules into linear bundles, microfibrils, is mainly caused by hydrogen bonding. The large number of hydrogen bonds gives rise to crystalline regions in the cell wall. The crystalline regions are interrupted by non-crystalline segments. A cellulose molecule passes through several crystalline and amorphous regions.

Hemicellulose molecules are also chain-like. Unlike cellulose, which contains only glucose, hemicellulose is composed of several kinds of monosaccharides. While softwoods contain 20 % glucomannan and only about 10 % xylan, hardwoods contain 5 % glucomannan and 25–30 % xylan, *i.e.* hardwood hemicelluloses contain considerably more pentose monomers. The hemicelluloses have low degrees of polymerisation, ranging from a few dozen to a few hundred monomers. Most hemicelluloses are branched, or have at least some side groups, *e.g.* there are many acetyl groups connected to hardwood xylans. They are soluble in alkali or even in water. Their structure inside the cell wall is believed to be that of a water-swelling gel.

Lignin is the major non-carbohydrate plant constituent. Chemically, it is quite different from cellulose and hemicellulose in that it is a very complex, cross-linked, three-dimensional macro-molecule made up of phenylpropane units. The aromatic nature of the phenolic units makes lignin hydrophobic and the three-dimensional structure provides rigidity for the cell wall. Molecular-weight determinations are difficult both to perform and to evaluate, since all isolation processes significantly change lignin constitution. Different kinds of biomass may be distinguished according to their content of guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) groups lignins (see Figure 1) [19]. Softwood contains mainly G-lignin, while hardwoods contain GS-lignins. Grasses contain all three forms of lignin. Any quantification of the lignin of a given plant must be considered as an average, since it has been found that lignin characteristics are different in different morphological units of the same plant.
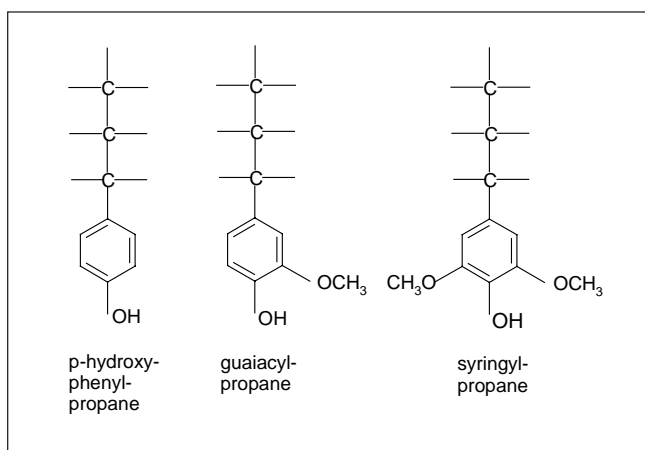
Figure 1 Phenylpropane units in lignin

The content of extractives as well as their chemical patterns can vary greatly between different wood species and also between different parts of the same tree. They are responsible for the characteristic colour and odour of many species, and, in some biomasses, for resistance to insect attack and decay.

2.1.1.1 Ashes

The ash composition and content varies considerably for different biomass feedstocks, as can be seen in Tables 2 and 3 [20]. The ash is mainly concentrated in the bark of woody materials, and ash content in agricultural biomasses and residues is higher than in wood. All the ashes mainly consist of calcium, silica and magnesium. The amounts of aluminium, iron and titanium are higher in woody biomass than in agrobiomasses.

Potassium is not really a trace component since its content in the ashes lies somewhere in the vicinity of that of silica and magnesium. The potassium and chlorine contents of the fertilized agrobiomasses are higher than those of wood; the 'K' in 'NPK' is often supplied as KCl [21]. Herbicides may also increase the chlorine content. Also phosphorous and sulfur are generally higher in the agrobiomasses.

For some species the time of harvest may influence concentration of ash components. Rainfalls during harvest may decrease chlorine and potassium contents [22]. If perennial species are harvested late enough in the autumn, they have relocated nutrients to the roots, *cf. Miscanthus*.

The temperatures in liquefaction are so low that the ash components react very little, except for sometimes being catalytically active. Thus the importance of the ashes in liquefaction is mainly physical. For example, if ash is not removed after dissolution of the raw material, remaining particles may foul catalyst particles in subsequent hydrotreatment.

Table 2 Ash analyses of selected biomass feedstocks [20]

	Ash analysis (g/kg)							
	Ca	Si	Mg	Al	Fe	Ti	P	S
Northern Woody Biomasses								
Wood chips	240	110	31.0	27.0	15.0	0.34	21.0	6.5
Forest residue chips (Finnish)	110	180	24.0	25.0	26.0	3.00	14.0	6.5
Forest residue chips (Swedish, high ash)	85	130	11.0	30.0	14.0	2.10	7.7	5.4
Saw dust (pine)	299	39	71.2	10.6	12.9	0.70	22.9	7.8
Spruce bark	280	7	31.0	5.7	1.0	0.21	18.0	3.9
Pine bark	290	6	27.0	28.0	2.1	0.46	21.0	8.2
Salix	220	2	31.0	1.6	1.3	<0.1	50.0	12.0
Agricultural biomasses								
Wheat straw (Danish)	52	280	11.0	4.3	3.8	0.25	9.9	4.4
Barley straw (Finnish)	32	290	13.0	<1	1.2	<0.1	11.0	5.7
Rapeseed	210	15	3.3	2.5	6.6	0.40	39.0	43.0
Flax (whole straw)	243	17	31.0	3.8	3.5	0.31	67.0	15.0
Reed canary grass	25	420	8.9	7.5	7.9	0.32	18.0	4.5
European biomasses								
Sweet *Sorghum* (Italy)	64	270	16.0	3.5	3.7	0.32	13.0	12.0
Kenaf (Italy)	220	31	36.0	9.4	8.5	0.49	12.0	23.0
Miscanthus (Italy)	54	200	29.0	2.7	2.8	0.20	23.0	8.4
Cane (Italy)	35	230	21.0	5.2	3.0	0.42	26.0	33.0

The temperatures in gasification are sufficiently high for some ash components to be problematic. Both chlorine and potassium are among those. When silica is present in the gasifier either from the biofuel (especially straw or rice husks) or in the bed (silica sand bed), its reaction with alkali metals is the main cause of ash sintering [21]. Silica reacts with unstable potassium compounds to form low-melting eutectics ($K_2O \cdot nSiO_2$).

However, if chlorine is present in high enough concentrations, potassium does not react with silica since KCl is more stable than K_2O but agglomeration in this case still occurs, though at higher temperature, and is controlled by condensation of KCl on particle surfaces. Silica also reacts with sodium-containing compounds.

Ash sintering may not necessarily lead to bed agglomeration. However, sintered ash can form clusters and insulate carbon compounds. For circulating beds, it has been reported that the fly ash may contain 40-50 % carbon, inducing a loss of efficiency [21].

Table 3 Amount of ash and trace components in of selected biomass feedstocks [20]

	Ash (wt % d.b.)	Trace components (ppm-wt, d.b.)		
		Na	K	Cl
Northern Woody Biomasses				
Wood chips	0.60	42	983	42
Forest residue chips (Finnish)	1.33	76	1377	76
Forest residue chips (Swedish, high ash)	4.05	640	2604	<50
Saw dust (pine)	0.08	20	480	<50
Spruce bark	2.34	89	3003	279
Pine bark	1.72	29	2133	85
Salix	1.18	37	4058	37
Agricultural biomasses				
Wheat straw (Danish)	4.71	140	5480	1710
Barley straw (Finnish)	5.88	333	12188	2737
Rapeseed	2.86	166	5768	965
Flax (whole straw)	2.93	133	5147	588
Flax (shive)	1.81	87	3362	381
Reed canary grass	8.85	154	3479	639
European biomasses				
Sweet *Sorghum* (Italy)	4.74	678	4614	2996
Kenaf (Italy)	3.63	517	7254	1748
Miscanthus (Italy)	3.31	259	9702	3266
Cane (Italy)	3.70	183	9706	2922
Miscanthus (Germany)	2.30	27	3027	1405

The concentration of HCl in the gas phase seems, thermodynamically, to depend not only on whether the bed in the gasifier is alkaline but also on the remaining ash constituents, on whether they in themselves are sufficiently alkaline [23].

Calcium, magnesium and phosphorus raise the ash melting temperature.

2.1.2 Moisture in biomass

Newly cut biomass usually contains about 50 weight % moisture [18] Most of this moisture will evaporate over a period of several months, but a point will be reached when no further moisture loss occurs. The biomass is then considered 'air-dried'; depending on relative humidity, the equilibrium moisture content may vary between 10 and 26 %.

The basic reason for moisture to enter into the biomass cell wall is the attraction of water molecules by the OH-groups of its chemical constituents. As a result, a layer of water is formed and held by these groups with strong hydrogen bonds. In

cellulose, the formation of this layer results in pushing apart the chains of cellulose molecules in the amorphous regions and between the crystallites of the microfibrils so that the biomass starts to swell. After saturation of the walls, the liquid water may also enter the cell cavities. The water held in the cell walls is called 'bound water' and that which is held in cavities is called 'free water'. The theoretical condition at which the walls are saturated but the cavities are empty is called the fibre saturation point. The moisture held in wood at the fibre saturation point varies between species, but on the average it is about 30 % of dry biomass weight.

The moisture content of biomass influences its glass transition temperature. The glass transition temperature, Tg, is a fundamental parameter for the physical characterisation of amorphous polymeric materials; it indicates the temperature region where materials change from a glassy to a rubbery state. The change to rubbery state is accompanied by reduced stiffness, so that materials well above their Tg at room ambient conditions will have rather different mechanical properties and behaviour than materials below it. For dry material, the Tg for cellulose is about 230 °C, 180 °C for hemicellulose and 200 °C for lignin [24]. Glass transition temperatures of polymers are significantly affected by plasticizers; water is a particularly important plasticizer for biomass components.

In completely dry biomass all components are well below their respective Tg. At the fibre saturation point, or above, the lignin is still below its Tg, while the hemicellulose and the non-crystalline portion of cellulose are well above theirs. Some of the components of wet biomass are therefore clearly in a rubbery state at room temperature, which helps explain the large dependence of mechanical properties on moisture content.

2.2 Peat

2.2.1 Peat formation

Peat is formed when plants are incompletely decomposed anaerobically. Peatlands are very common in glaciated areas where the groundwater table is close to the surface, *i.e.* in Scandinavia, Russia, Canada and the United States [7]. Peat characteristics differ depending on locale and the type of decayed plants. Content and composition of ashes also vary depending on the surroundings.

In ombrotrophic peatlands the water is supplied exclusively by precipitation while minerotrophic mires are supplied with water from surrounding mineral soil as well.

Fens are minerotrophic mires. Fens may be found on the surface of lakes which have been filled with plants. The natural growth of aquatic vegetation occurs more rapidly in areas where the soil is naturally rich in nutrients, for example in clay areas. If the clay at the bottom of the fen is nutrient-rich, the fen is often used for agriculture, thus disappearing from the landscape [25].

In Sweden, though, embogged peatlands are the most common. Where the groundwater table is high, near natural springs and on rainy slopes, *etc.*, embogging

on mineral soils is common. Whenever embogging appears, recent vegetation will be 'drowned' by vegetation requiring wetter conditions [26].

The fen may then either be nutrient-rich and brown moss-dominated (*Bryales*), or nutrient-poor and *Sphagnum*-dominated (reindeer moss). Remains of reeds (*Phragmites*) and sedges (*Carex*) as well as alder and birch may also be found in the layers of nutrient-rich peat. The nutrient-poor fens are less diverse, with remains of sedges, Arctic (dwarf) birch and fir besides *Sphagnum* [5]. If the fens are allowed to grow, they finally become raised, ombrotrophic bogs. These are only to be found in moderate to cold climates and are independent of the layers below; they are *Sphagnum*-dominated. They have an autonomous water system, based on rainwater and regulated only by evaporation and precipitation [7].

2.2.2 Peat humification

The degree of decomposition, or humification, may be measured in various ways [7, 27]. A common method for physical characterisation [28] is the von Post scale, where H1 denotes completely unhumified and mud-free peat. When squeezed by hand only uncoloured, clear water is released. H10 denotes completely humified or mud-like peat, with no discernible plant structure. When squeezed, the whole peat sample oozes out, without any free water being released. H1–H6 peats are known as white peats while black peats refer to samples of humification H7-H10 [25]. Table 4 shows how elementary analysis and ash content may vary with degree of humification for some Swedish peats [29].

Table 4 Degree of decomposition, elementary analysis and ash content of some Swedish peat samples [29]

Peat sample	Degree of decomposition	Elementary analysis*				Ash content (wt %)
		C	H	N	O (by diff)	
Hasselfors	H3	51.0	5.6	0.6	42.8	0.6
Bredsjö (Järlåsa)	H4-5	52	5.6	0.4	42	1.9
Hummelstorp (Sorunda)	H4-5	53.5	5.7	0.7	40.1	0.7
Hummelstorp (Sorunda)	H5	53.9	5.5	0.7	39.9	0.8
Sösdala	H6	56.6	5.2	0.7	37.5	1.1
Sösdala	H7	57.7	5.5	1.0	35.8	1.2
Uggelstam (Nävekvarn)	H7-8	56.2	6.3	3.5	34	39.5

* dry ash-free peat

With increasing peat age, the degree of humification increases though more and more slowly. After death, the initial decay of the plants is areobic. Then, more plant material grows and is accumulated above the decaying layer which may grow to a thickness of 10-50 cm. The structures in the decaying layer then collapse; the void fraction decreases and bulk density increases while hydraulic conductivity, *i.e.* the ability to transport water, decreases [30, 31]. This collapse layer has a thickness of 2-15 cm. The layer below also has a high density and low hydraulic conductivity; most of it is permanently water-logged. The height of the water table varies during the year, from slightly below the collapse layer to slightly above it. Since oxygen diffusion through water is slow, conditions slightly below the water table become anaerobic as the oxygen that does flow into the water is consumed near the upper limit by oxidation of organic matter aided by microorganisms [7]. Further decay is then much slower. Table 5 shows a summary of the effects of age. Carbon content in peat increases and oxygen content decreases as the content of hemicellulose and cellulose decreases.

Among the peat-forming plants, mosses, liverworts and such do not possess lignin, but do have chemically similar substances performing the same functions as lignin. During plant decomposition, lignin is relatively stable [27]. But it is also, by some, regarded as the precursor of humic acids, which constitutes a major fraction of peat. This, in the case of peat, is supported the fact that the fungi that degrade lignin are not normally found in excessively wet sediments [32]. Others consider humic acids to be a microbial product derived largely from other components in the decomposing plant. Like lignin, humic acids have phenolic elements in their structure, but unlike lignin, humic acids have a high carboxylic acid content and contain significant amounts of nitrogen [27].

Ash content increases, or rather, the organic content decreases, with age. Minerotrophic peatlands generally contain higher amounts of ash than ombrotrophic peatlands. The ash content not only reflects the ashes of the peat-forming plants, but also the remains of the peat-decomposing organisms. As long as the peat is formed minerotrophically, there is contact with the surrounding groundwater, and the minerals in the surroundings may influence ash content [33].

The fats and waxes of the extractive portion of the original plant material of peat tend to be quite resistant to decay and fungal and bacterial attack.

Peat in the bog may contain more than 90 % water. It can be mechanically dewatered to about 30 % dry substance while the different peat harvesting methods

Table 5 Summary of the effects of age on the most important chemical and physical characteristics of peat [7]

	Increases/Decreases with age
C-content	+
O-content	-
Carbohydrate content	-
Lignin and recalcitrant matter	+
Ash content	+
Bulk density	+
Pore fraction	-

utilize wind and sunshine (whenever available) for drying to 35-50 % dry substance, allowing the peat to be transported for further processing.

2.2.3 Peat characteristics

The energy content per weight unit in dry moisture-and ash-free peat not only reflects the degree of humification, with more highly humified peats being more energy-rich, but also the composition of the constituting plants [34]. This can be seen in Figure 2 where heating values are plotted as functions of the degree of humification for various types of peat. The high-moor peats (*Sphagnum*) have the lowest heating values and those derived from wood have the highest. In this graph a Sphagnum peat of H8 humification has the same heating value as a low-moor (*Carex*) peat of only H3.

Thus, a low ash content and a high degree of humification are not sufficient criteria for the selection of peats appropriate for thermochemical processing. Much work has been performed in Russia on characterization of peat as to suitability for pyrolysis and wet carbonization.

Based on their degree of humification, ash content, heat of combustion and pH, the chemical group composition of a number of peat samples was calculated within the framework of the 'Oil from Peat' project [3, 35]. Different types of peat were then analysed as to content of bitument (B), humic acids (HA), nonhydrolysables (NH), water solubles and easily hydrolysables (WSEH) as well as fulvic acids (FA) and cellulose (Cell), see Table 6.
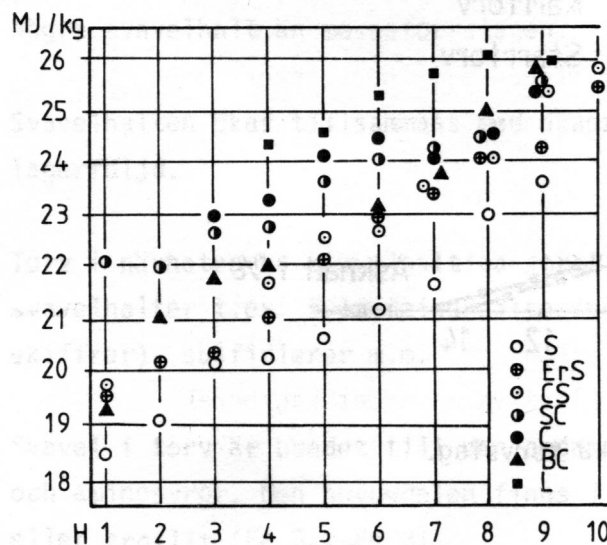
Figure 2 Heating values (dry and ash-free) for increasing humification for different kinds of peat as function of main peat raw materials: S *Sphagnum*; ErS *Eriophorum Sphagnum*; CS *Carex Sphagnum*; SC *Sphagnum Carex*; C *Carex*; BC *Bryales Carex*; L wood remains [5]

Table 6 Principal group components in peat and their composition and/or structures [34]

Component	Typical chemical compounds and/or structures in peat components
Bitumen (B)	Waxes, resins (acids, alcohols, polymeric products, terpenes), paraffins and sterols; High concentration of $-CH_2$ structural units
Humic acids (HA)	Condensed aromatic, hydroaromatic and heterocyclic structures; Functional groups in decreasing order of content: carboxyl, carbonyl, phenolic hydroxyl, alcoholic hydroxyl
Nonhydrolysables (NH)	Three-dimensional polymer of phenylpropane units; Functional groups: carboxyl, methoxyl, alcoholic hydroxyl, phenolic hydroxyl, carbonyl
Water solubles and easily hydrolysables (WSEH)	Hemicelluloses, glycosides, pectins; Polysaccharides built up of different hexoses, pentoses, and uronic acids
Fulvic acids (FA)	Extracted along with HA (with NaOH) and not precipitated on acidification; FA contain less C and more H than do HA
Cellulose (Cell)	Polysaccharide, polymer of glucose

It was found that B, HA and NH are the main coke and tar-forming peat constituents. This was accomplished using linear regression equations proposed by Lishtvan and Korol [36]. The results obtained were used as tools for interpreting the outcome of experiments already performed at KTH on liquefaction of raw peat samples at 355 °C under 8.3 MPa CO, with 0.14 g K_2CO_3/g dry feed.

The total yield of toluene-soluble and toluene-insoluble products was found to be proportional to the total amount of bitumen, humic acids and nonhydrolysables in the raw material [34]. The lower the rank of the raw material and the higher its H/C ratio, the higher is the ratio between the soluble and insoluble fractions in the products.

The yield of desirable products obtained from some slightly humified low moor products may thus be higher than would be expected from only the low degree of humification.

3 PYROLYSIS, LIQUEFACTION AND GASIFICATION

Both liquefaction and gasification are thermal conversion methods for producing higher-value liquid and/or gaseous fuels and/or chemicals, usually from solid raw materials. The present technologies for both liquefaction and gasification of peat and biomass are developments of technologies originally developed for coal.

3.1 General

3.1.1 Pyrolysis

Pyrolysis is the initial step in all thermal conversion of carbon-containing materials and has great importance for the basic understanding of further conversion processes. The term denotes both a sequence of reactions, and is the generic name of a number of processes. It is the sequences of reactions that are treated here.

The pyrolysis products vary not only depending on raw material composition, but also very much depending on particle size, heating rate and final temperature.

3.1.1.1 Cellulose

Even at temperatures as low as 70 °C, cellulose begins to slowly decompose generating a gas composed of 90-95 % CO_2 and 5-10 % H_2O (by volume) [37]. Below 250 °C, the major products of cellulose pyrolysis are H_2O, CO, CO_2 and char. The degree of polymerization undergoes a rapid drop to a steady value of about 200 during the early stages of pyrolysis. Bond rupture occurs at points of maximum strain in the polymer along the boundary where the crystalline and amorphous regions meet. Weight loss during decrease of DP may be 5-10 %, and after this initial weight loss, levoglucosan formation increases.

The initial weight loss is probably due to cross-linking in the amorphous region (dehydration). Crystalllinity is increased with annealing; with increased temperature, the cellulose chains in the amorphous regions are freer to align themselves to favour cross-linking.

Levoglucosan probably derives mostly from crystalline regions (at higher temperatures acetaldehyde). Furfural and hydroxymethylfurfural probably come mostly from the amorphous regions.

There is also a random bond cleavage both in the crystalline and non-crystalline regions. The mechanism has been quoted as either hydrogen free radical leaving or carbonium ion.

A global model for the degradation of cellulose could be:

1   At low temperatures those reactions dominate which lead to elimination of water, CO and CO_2 as well as formation of carbonyl and carboxyl groups, the appearance of free radicals and, finally, char.

2   Above 300 °C the second pathway gradually begins to dominate. The primary reaction is depolymerization by transglycosylation, giving levoglucosan, its furanose isomer and randomly linked oligosaccharides.

3   The third reaction is fission and disproportionation yielding gases and low molecular weight products. At low temperature it may only be a variety of the dehydration reaction.

Noncellulosic carbohydrates undergo thermal degradation at lower temperatures than cellulose but the pyrolysis phenomenology is very similar. Especially the thermal reactions of the carbohydrates of importance for the food industry have been studied.

3.1.1.2 Lignin

The rate of thermal degradation of lignin is very slow below 200 °C [38]. The relatively high glass transition temperature is attributed in part to the role of intermolecular bonding due to the OH groups present in lignin.

It has been shown that the method of lignin isolation only influenced the distribution of products formed in the 100 to 200 °C temperature range. Products formed at 300 °C were identical for all types of lignin studied.

Diffential thermogravimetric studies have been made of phenylpropanoic compounds (see Figure 1). Those with only single-bonded carbon atoms in side chain underwent cleavage and dehydration whereas guaiacylpropenol polycondensed at 240 to 300 °C, and the condensation products underwent further degradation at 380 °C in a manner resembling noncellulosic carbohydrate pyrolysis.

The variety of gases, condensable compounds and char formed during the moderate temperature pyrolysis of lignin is remiscent of the behaviour of carbohydrates. However, no set of conditions has been discovered which leads to the depolymerization of lignin and the formation of a high yield of 'monomer'.

At low heating rates the char yield from lignin exceeds 50 % by weight, with elemental formula $(C_{40}H_{38}O_{11})_2$. Water, methanol (more from hardwoods than softwoods), acetic acid, acetone and acetaldehyde are the major components of the aqueous distillate. The tars, 15-20 %, are composed of a variety of compounds related to phenols, all in low concentration. Lignins isolated from softwood are more stable than those isolated from hardwood.

Increasing pyrolysis temperatures decrease the observed yields of char, while enhancing the formation of condensable products and/or gases, depending on reactor conditions.

3.1.1.3 Whole wood

In one study the effect of lignin content on the thermal degradation of wood pulp was studied. An increase in the lignin content of pulp from 3.7 to 23 % was observed to dramatically reduce the activation energy. The nonlinear effect may be a result of phenols being active free radical traps, while free radicals play a role in cellulose pyrolysis [38].

Thus, the components of wood seem to interact in pyrolysis. The overall patterns of the three major pathways noted in the components are preserved in the pyrolysis of composite lignocellulosic material. At low temperatures, condensation reactions give rise to the formation of charcoal. At higher temperatures transglycosylation and similar reactions result in the formation of tar and some gases. Above 500 °C, vapour phase cracking reactions convert the reactive vapours evolved by the solid-phase pyrolysis reactions into a hydrocarbon-rich synthesis gas, while competing vapour-phase condensation reactions form refractory condensable materials.

3.1.1.4 Coal

Many recent studies have suggested that coal, though a generic name for widely differing materials, can be thought of as having a macromolecular network structure, which includes unbound guest molecules. Thermally stable aromatic ring clusters are connected by weaker bridges; there are also long-chain aliphatics present [39].

As the coal is heated there are three processes, which occur in the temperature range 200–400°C prior to pyrolysis. These processes are disruption of hydrogen bonds, vaporisation and transport of non-covalently bonded 'molecular phase' and a low-temperature crosslinking in coals with more than 10 % oxygen, which coincides with CO_2 or H_2O evolution [40].

During primary pyrolysis, the decomposition releases large molecular fragments by depolymerisation due to rupture of weak bridging bonds. Most of these bonds are broken homolytically, giving rise to free radicals [14]. Model compound studies suggest that the C—O bond of benzylic ethers and the C—C bond of ethylene bridges connecting aryl groups are prone to low temperature bond scission. The fragments formed are resonance stabilized. Substituents on an aromatic ring may also decrease thermal stability considerably.

The formed radicals abstract hydrogen from the hydroaromatics or aliphatics, thus increasing the aromatic and the olefinic hydrogen concentration. A simplified scheme may look as follows:
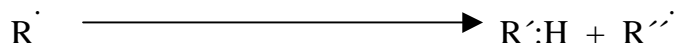
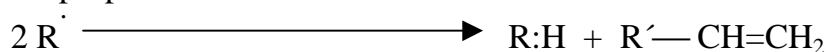1 Thermolysis of bond within the coal matrix

$$R:R \xrightarrow{\text{heat}} R^{\cdot} + R^{\cdot}$$
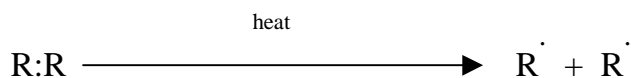
2 Addition of hydrogen from internal or external source

$$R^{\cdot} + H^{\cdot} \longrightarrow R:H$$

3 Fragmentation

$$R^{\cdot} \longrightarrow R':H + R''^{\cdot}$$

4 Disproportionation

$$2 R^{\cdot} \longrightarrow R:H + R'-CH=CH_2$$

5 Coupling to form coke or char

$$R^{\cdot} + R^{\cdot} \longrightarrow R:R$$
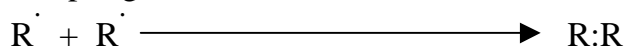
The fragments can be released as tar if they are small enough to vaporize and be transported out of the char particle without undergoing moderate temperature crosslinking reactions before escaping from the particle. The decomposition of the individual functional groups, which release gases, mainly CO_2, light aliphatic hydrocarbons and H_2O occurs simultaneously with the depolymerization. Primary pyrolysis ends when the donatable hydrogens from hydroaromatic or aliphatic portion are consumed.

The product distribution among the coal tar fractions is highly dependent on the nature of the coal being pyrolysed. The pyrolysis of lignite, for example, yields a much higher proportion of alkanes, alkenes and cycloalkanes than does a similar pyrolysis reaction of a higher-rank coal. Also, the aromatic component of lignite contains less highly condensed material (typically one or two rings) than does the aromatic material from higher-rank coal [14].

During the secondary pyrolysis there is additional gas formation, methane evolution (from methyl groups), HCN from ring nitrogen compounds, CO from ether links, and H_2 from ring condensation [39].

Devolatilization of coal results in mass loss from the solid material to form char, and the evolution of gases and tars. Gas formation can often be related to the thermal decomposition of specific functional groups in the coal and can be predicted with reasonable accuracy. Tar and char formation are more complicated. It is generally agreed that tar formation includes the following steps:

1   Depolymerization by bond rupture of weaker bridges in the coal macromolecule to release smaller fragments that make up the 'metaplast'.

2   Repolymerization of metaplast molecules.

3   Transport of lighter molecules away from the surface of the coal particles by combined vaporization, convection and gas-phase diffusion.

4   Internal transport of molecules to the surface of the coal particles by convection and diffusion in the pores of non-softening coals and by liquid-phase or bubble transport in softening coals.

Char is formed from the unreleased or recondensed fragments. Various amounts of loosely bound 'guest' molecules are also released in devolatilization. The rate of escape of the tar decreases with increasing pressure, this implies a longer residence time of tar precursors in the particle, allowing a larger fraction to be repolymerized into the char structure. Once reincorporated into the matrix by more stable bonds, the tar precursors can yield volatiles only by reactions that break them into smaller molecules or split off small side groups. These reactions lead to lower tar yields because small molecules require more donated hydrogen per unit mass for radical-capping than large molecules do.

3.1.2 Liquefaction

The pyrolytic breakup of the coal matrix begins above 400 °C. As described in the section on pyrolysis, a large number of concurrent and competitive chemical reactions occur during the liquefaction process, *i.a.* thermolysis, hydrogen abstraction, dealkylation, cleavage of bridges between structural units; there is also desulfurization, dehydration and ring opening [14].

Once one or more of the weaker coal bonds has been cleaved, the free radicals generated can, instead of reacting further in the way they would under pyrolytic conditions, be stabilized by the addition of hydrogen. The hydrogen may be added either from molecular hydrogen or from a hydrogen-donor solvent. If a donor solvent is used, it must also be able to dissolve the stabilized fragments [41]. Yet another property a good liquefaction solvent should have is the ability to be easily rehydrogenated, thereby allowing 'shuttling', which is abstraction of hydrogen from hydrogen-rich areas of the coal and donating them wherever there is hydrogen deficiency.

Partially hydrogenated aromatic compounds have been found to be good hydrogen donors, i.e. tetralin and its homologues, partially hydrogenated pyrene, phenanthrene and other polycyclic aromatic compounds [42].

Effective solvents for coal liquids must contain polar compounds, such as phenols, pyridines, aromatic ethers, quinolines and their derivatives. Good solubility in the solvent of the coal fragments being dissolved is also important in that components
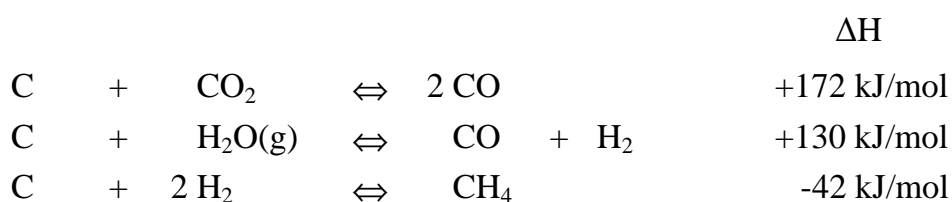
which are insoluble in a mixture will tend to self condense, forming coke at a faster rate than if they were freely dispersed in the medium. Also, high solubility aids in transporting material in and out of solid catalysts, including coal mineral matter.

Hydrogen shuttling is accomplished by solvent components which are good H-acceptors, as well as H-donors. For example naphthalene acts as an H-acceptor, and the resultant free radical formed by the addition of an H-atom acts as an H-donor. Phenanthrene and pyrene are among the H-acceptors which are more efficient than napthalene. Alkyl derivatives of the three compounds are also good H-acceptors.

It should also be kept in mind that some solvent components promote char formation, such as heavy phenols and highly aromatic compounds.

3.1.3 Gasification

Also gasification begins with pyrolysis giving a solid residue, char, consisting mainly of carbon and ash, a gas phase and a condensable phase consisting of tar and water. Char conversion takes place through the true gasification reactions, the main ones being [43]:

$$\Delta H$$

$$C + CO_2 \Leftrightarrow 2\,CO \qquad +172 \text{ kJ/mol}$$
$$C + H_2O(g) \Leftrightarrow CO + H_2 \qquad +130 \text{ kJ/mol}$$
$$C + 2\,H_2 \Leftrightarrow CH_4 \qquad -42 \text{ kJ/mol}$$

The first two reactions are the main gasification reactions, showing that gasification consumes energy; the third reaction only occurs for high hydrogen partial pressure. The energy is usually obtained by oxygen reacting with part of the char according to the following:

$$\Delta H$$

$$C + \tfrac{1}{2}\,O_2 \Leftrightarrow CO \qquad -109 \text{ kJ/mol}$$
$$C + O_2 \Leftrightarrow CO_2 \qquad -390 \text{ kJ/mol}$$
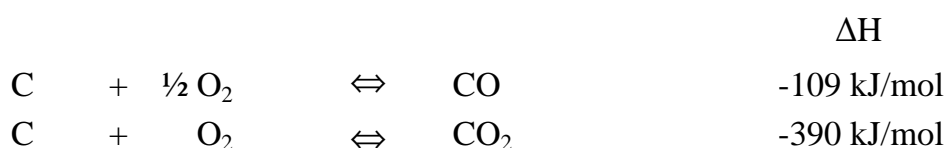
The amount of oxygen added is usually expressed as the equivalence ratio, i.e. the air-to-fuel ratio used divided by the-air-to-fuel ratio of stoichiometric combustion [44]. For biomass gasification it is about 0.20 to 0.35.

As can be seen from the last two reactions above, the added oxygen preferentially reacts with the char. A large part of the tars formed are neither combusted nor thermally cracked; usually the produced gas requires further processing downstream to decompose these tars into lighter compounds. The tars are much more of a problem in biomass gasification than in the gasification of coal. The higher reactivity of biomass, allowing lower reaction temperatures, results in

considerably larger amounts of tar remaining in the produced gas at the outlet of the reactor.

Evans and Milne have suggested that a systematic approach to the classification of pyrolysis products from biomass as primary, secondary and tertiary might be useful [45]. They used molecular beam mass spectrometry to characterize vapours from wood pyrolysis in helium with a gas phase residence time of 300 ms, varying the final temperature from 500 to 1000 °C. The results obtained are shown in Figure 3. Destruction of primary products begin before tertiary products appear. The tertiary aromatics were formed from cellulose as well as lignin although higher molecular weight aromatics were formed faster from the lignin-derived products. The four kinds of product shown in Figure 3 are:

1   Primary products from cellulose, hemicellulose and lignin.

2   Secondary products characterized by phenolic peaks.

3   Alkyl tertiary products that include derivatives of aromatics.

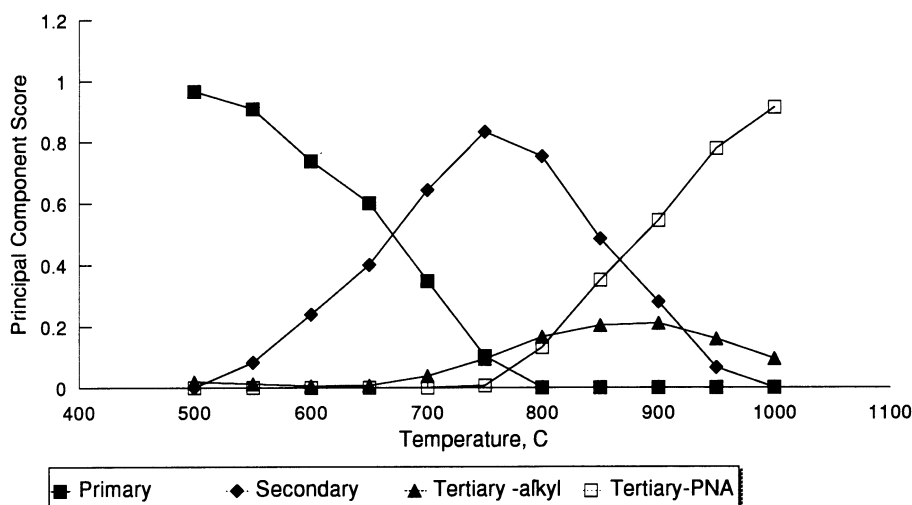4   Condensed tertiary products that show the polynuclear series without substituents.

Figure 3 The distribution of the four tar components as a function of temperature for the 300 ms residence data set, from [45]

3.2 Process development

3.2.1 Coal liquefaction

3.2.1.1 Direct conversion

The two main routes for producing oil from coal both originated in Germany. The hydrogenation or direct conversion process, which converts coal directly into

liquids, was the first to be discovered, by Bergius in 1913 [46]. This two-stage process supplied the Germans especially with aviation fuel during World War II [47]. It involved catalytic conversion of coal slurried with heavy oil, with Fe_2O_3 and Na_2S added, at a hydrogen pressure of 300-700 atm. The lower pressure was used when lignite was used as input instead of bituminous coal. The products were usually separated into light oils, middle distillates and residuum. The oils except the residuum were catalytically cracked in a vapour-phase hydrogenation step, the second stage of the process. The process contributed greatly to the development of catalytic coal liquefaction technology [48].

Both single-stage and two stage processes for coal liquefaction have later been developed. The distinction between them is not always very clear [49, 50].

Single stage liquefaction

Especially during the 70's there was renewed interest in coal liquefaction and a number of processes came to reach the pilot plant stage. Some of these are shortly described.

Bergbau-Forschung Coal Hydrogenation Plant [49]: An experimental plant at Essen began running in 1979. Experimental results were used for design and construction of the Kohleöl-Anlage Bottrop (scale-up >1000). Typical experimental conditions were 300 bar, 475 °C (after preheating to 420 °C), coal:recirculation oil (100% distillate) 0.7, red mud as catalyst and gas flame coal from Ruhr as raw material.

There was a major, important difference between the sump phase hydrogenation according to Bergius/Pier and the coal-oil process derived from it. Whereas formerly the majority of the pre-asphaltenes and asphaltenes were recycled to the process as constituents of the recycle oil, a distillate was used in the newer process. Decreasing the operating pressure to 300 bar instead of 700 bar was the principal benefit of this change.

In 1983 Bergbau-Forschung began development of a process with integrated refining of the raw coal oil. Before condensation of the coal oil leaving the top of the intermediate separator as vapour, the temperature was increased to 380 °C and the mixture passed through a reactor with a fixed bed Ni-Mo/Al_2O_3 catalyst. This operating mode was maintained for several weeks without much catalytic activity loss. The refined coal is stabilized and storable.

An incentive for studying coal liquefaction in the US was from the beginning desulfurization of high-sulfur coals, especially from the eastern US.

H-Coal is a direct catalytic coal liquefaction process developed by Hydrocarbon Research, Inc. (HRI). Coal, recycle liquids, hydrogen and Co-Mo catalyst are brought together in an ebullated bed reactor to convert the coal into hydrocarbon liquid and vapour products. The process converts a wide variety of coals into different product slates, depending on operating conditions, but, like all-single stage processes, H-coal is best suited for volatile bituminous coal [48].

The EDS (Exxon Donor Solvent) process was developed 1976-1985. The use of a separate reactor for hydrogenation of the recycle solvent is a key feature of the process. The solvent is used as a donor of hydrogen to the slurried coal, at 175 bar, >425 °C. Conventional petroleum technology is used for hydrogenating the solvent.

The process can be used for bituminous (39-46 % liquids), and subbituminous coals (36 %) as well as for lignites (36 %). Liquefaction yield can be increased substantially by recycling vacuum bottoms back to liquefaction.

Development work on the SRC-I (Solvent Refined Coal) process was initiated in 1966. The principal objective of the original SRC-I process was a solid boiler fuel with a melting point of about 150 °C and a heating value of 37 MJ/kg. It is a thermal liquefaction process in which solvent (all distillate liquid), coal and hydrogen (hydrogen-rich recycle gas) are reacted in a 'dissolver' at 455 °C, 100 bar to produce a non-distillable resid, which upon de-ashing can be used as a clean boiler fuel (95 % of daf coal dissolved). This process is ideally suited for bituminous coals especially those containing high concentrations of pyrite, which is considered to be the liquefaction catalyst. Non-distillable SRC-I products cannot be deashed by vacuum distillation. Extracton type separation processes were developed specifically for this process. Typical of these is Kerr-McGee's critical solvent deashing (CSD) (see below).

In the SRC-II process a portion of the dissolver product slurry is recycled as a 'solvent' for the coal rather than using an all-distillate liquid. The amount of mineral matter in the coal, which is the only catalyst, is thus kept high high by this recirculation. This and the more severe reaction conditions (140 bar instead of 100) distinguish SRC-II from SRC-I. The net product is -540 °C distillate, recovered by vacuum distillation. Vacuum bottoms, including ash, are gasified to supply process hydrogen.

The process is limited to coals containing 'catalytic mineral matter' and therefore excludes all lower rank coals and some bituminous coals. Solvent-to-coal ratio is 2 for SRC II while it is 1.5 for SRC I. The change in product distribution resulted in a higher hydrogen consumption (4-5 % of the coal feel) compared to SRC-I operation (2 % of coal feed).

Two- stage liquefaction

The LSE (Liquid Solvent Extraction) process was developed by British Coal at the Coal Research Establishment in Cheltenham [50]. Ground coal is mixed with a process-derived solvent to give a slurry containing up to 40 % of coal by weight. The slurry is preheated and passed to digester, *i.e.* two continuous stirred tank reactors in series. Pressurization is only enough to reduce solvent vaporization. The solvent acts as a hydrogen donor, transferring up to 2 % by weight of hydrogen to the coal. Small amounts of gas and light distillate are produced during extraction and are removed via an atmospheric column.

The Wilsonville, Alabama, ITSL (Integrated Two-Stage Liquefaction) processes started operating in 1970. Although originally built as a pilot-plant for the SRC-II process, an ebullated bed hydrocracker was added in 1981. Several different configurations of the ITSL process were then tested [48].

Ground coal is mixed with a process-derived solvent to give a slurry containing up to 40 wt % coal. It is pressurized, mixed with hydrogen and preheated before passing to the dissolver, a simple unstirred vessel. The products are fed to a high-pressure separator, the gas is scrubbed and a purge stream is flared, the remainder being recycled. The hydrogen content of the recycle gas is maintained at 85 % by volume.

The bottoms from the high-pressure separator contain light distillates, solvent-dissolved coal (known as thermal resid, TR), undissolved coal and mineral matter. The pressure is first lowered to 14 bar, then the products are fed to a vacuum column, whose bottoms pass forward to the de-ashing unit as a hot, viscous slurry.

Kerr-McGee specially developed a process (CSD, critical solvent deashing) for this type of undistillable material. Process parameters are thought to be about 325-340 °C, 50 bar and a solvent-to-feed ratio of 5:1. Mixing of slurry and aromatic solvent takes place at conditions close to the critical point of the solvent, the temperature is then raised.

The mixture is fed to the first stage settler. Mineral matter and undissolved coal are insoluble in the deashing solvent and are removed from the settler in the underflow, from which the deashing solvent is recovered by depressurizing the mixture. The ash concentrate produced in this way is a free-flowing powder.

Light distillates, or a combination of thermal residue and light distillates, are blended with process solvent to produce a pumpable liquid. Hydrogen is added and the mixture is preheated before passing to the ebullated bed hydrotreater. The reactor is operated with a high proportion of recycle to maintain the catalyst bed in a highly expanded state.

In 1982, HRI began the development of a two-stage process, CSTL (Catalytic Two-Stage Liquefaction), to overcome the shortcomings of the H-coal process. The first stage temperature was lowered to 400 °C while the second stage was operated at higher temperatures to promote resid hydrocracking and generate an aromatic solvent which is then hydrogenated in the first stage [48]. A pressure filter was added to reduce resid concentration in the filter cake. The catalyst was also changed, from Co-Mo to Ni-Mo with larger micropores, more suitable for the large molecules dissolved from coal.

In all processes where US and European coals were compared, it was found that the geologically younger US coals react more easily.

3.2.1.2 Indirect conversion

The indirect conversion method is called indirect since the coal is first gasified, and then the produced gas is synthesized into liquid products. It was patented in 1925 when Fischer and Tropsch published their finding that passing a gas consisting of carbon monoxide and hydrogen over a cobalt catalyst produced a product similar to oil [46]. It was soon found that though the process was interesting for the production of motor fuels, the primary products from the synthesis, using a cobalt catalyst, were better suited as raw materials for chemicals.

The gas used by most of the F-T plants in the 30's and 40's came from coke ovens. However, in the 30's Lurgi was already developing gasifiers in which oxygen (as well as steam) was blown, raising temperature and pressure, *i.e.* increasing throughput.

F-T synthesis is used in the South African SASOL units, after Lurgi gasification, for production of most of the country's requirements as to automotive fuels and chemicals. In the first SASOL unit, a so-called 'Arge' fixed-bed reactor was used. Instead of a cobalt catalyst, a pellet-shaped iron catalyst packed in long narrow tubes surrounded by boiling water was used. Also fluid bed technology with circulating catalyst, which came to be known as Synthol, was employed. Synthol produces more olefins and gasoline than the fixed bed, which normally yields more diesel and waxes. Further SASOL units use the Synthol technology.

The South African SASOL development is special in that it was a state-owned enterprise operating under special political conditions, using cheap labour. However, it managed to become economically successful, and is now listed on the Nasdaq stock exchange.

Synthesis gas may not only be produced from coal, but also from natural gas, naphtha (for both these feeds the synthesis gas is produced by steam reforming) or heavy residues (synthesis gas produced by partial oxidation). Methanol may then be produced by the catalytic conversion of synthesis gas containing carbon monoxide, carbon dioxide and hydrogen as the main components.

There are also processes for the production of gasoline and distillate fuels, via methanol, from natural gas. In the early 70's Mobil discovered a new family of medium-pore zeolites (5-6 Å) [46]. This led to the development of both the MTG (Methanol to Gasoline) and MOGD (Mobil Olefin to Gasoline and Distillate) processes [51]. The MTG process is in commercial operation in New Zealand.

Fischer-Tropsch synthesis may also be used on synthesis gas generated from natural gas. An example is the SMDS (Shell Middle Distillate Synthesis) process in operation in Malaysia. The F-T product has a large fraction of waxy product which is cracked, via an appropriate zeolitic catalyst, to the molecular weight distribution required for gasoline. The advantage is that the gasoline does not contain any aromatics [52].

3.2.2 Biomass liquefaction

There are many ways of producing combustible liquids from biomass. In this section, however, only some of the concepts developed for direct thermochemical liquefaction of unfractionated biomass are discussed.

3.2.2.1 Direct conversion

The demonstration plant completed at Albany, Oregon, in December 1976 is special in that it is the only relatively large-scale biomass liquefaction plant, originally designed for 3 t/d of (dry) wood, built so far. It came to be used for the testing of two concepts.

Originally, the facility was intended for scale-up demonstration of work performed at The Pittsburgh Energy Research Center (PERC) of the US Bureau of Mines [53]. However, possible severe limitations of the proposed concept were identified early, so the process evaluated was an adaptation to biomass feedstocks of a CO-steam process originally developed for lignite. The process was still called the PERC process, though.

Wood, ground to a fine powder, was mixed with recycled product oil (ratio 1:9) and then blended, at about 100 °C, with water containing sodium carbonate (20 % aqueous solution, to give 2-6 wt % of dry wood). The mixture was heated in a reactor equipped with a stirrer prior to entering the reactor, where CO and H_2 were introduced. After cooling and pressure letdown, a portion of the wood-oil was withdrawn as a product and separated from the aqueous effluent. The remaining oil was recycled, without separation of the water, to the wood flour blender. In the absence of wood-derived oil, anthracene was used as the initial slurrying medium.

The system was designed to treat the slurry with synthesis gas at about 28 MPa, 370 °C, with a flow of reducing gas (3 to 6 wt %) for 0.5 to 1.5 h.

The design of the unit was intended for the biomass feed to be slurried at 30 wt % solids in recycled product oil, but as the recycle was very viscous, the actual feed was less than 10 %. This gave very low, economically unfeasible, productivity.

There were many practical problems besides insufficient knowledge about reaction chemistry. Still, almost 5000 l of nearly pure wood-derived oil (with a yield of over 53 % of dry wood feed) was produced during almost 600 h of operation, after several years besieged with difficulties.

The Lawrence Berkeley Laboratories (LBL) in California modified the PERC process concept and tested it, also at Albany. The LBL process was a once-through process where the wood was prehydrolysed in very dilute aqueous sulfuric acid, eliminating the grinding requirements and pumping problems of the PERC process. Sodium carbonate was then added to the mixture, to a pH of about 8. This allowed slurries of 30-33 wt % wood chips to be pumped through a tubular heater similar to the one used in the PERC process. The reaction thereafter took place in a turbulent

tubular reactor or in a well-stirred reactor. Conditions closely matched those of the PERC process.

Low oil yields were obtained, while there was a high yield of water-solubles, making the process economically unfeasible.

A basic problem for both concepts at Albany was to get the biomass into the liquefaction reactor at high concentration and high rate without deteriorating product distribution, and without mechanical problems.

An interesting approach to resolving the above problem was made at the University of Arizona where a modified polymer extruder was used for feeding the slurry into the reactor. The extruder not only provided a continuous feeding system, it could also pump 60 wt% wood flour in recycle oil. The products obtained are similar to those obtained in the PERC process, with higher oxygen content and greater acidity than for fossil oils.

This work was discontinued in 1988, both because analysis of the PERC process had shown that liquefaction could not be economically attractive and because US priorities shifted away from high-pressure liquefaction.

The idea of the extruder was taken a step further by work at the University of Saskatchewan; an auger was used there, both for feeding the raw material and for passing it through the reaction zone. Just prior to the water injection point, at 360 °C, the air-dried wood meal formed a plug capable of withstanding 10 MPa pressure. Thus gas, usually CO, could be added downstream the water, without the water escaping 'backward' and condensing in the wood meal hopper.

Various variables were investigated. Most important seemed to be the water:wood ratio (varied from 0.5:1 to 5:1); the oil yield (35 to 56 wt%) was inversely proportional to this ratio. No effect was found for variation of temperature, 320 to 360 °C, initial CO pressure, 5.2 to 8.6 MPa, or variation of catalyst content, 7.5 to 12.5 wt% sodium or potassium carbonate and potassium hydroxide.

Rapid hydropyrolysis of powdered wood was studied at the University of Toronto [54]. Conversion was about 95 % after heating to 350 °C in 70 to 90 s followed by immediate quenching. These studies were followed by studies of poplar chips at a water:wood ratio of 3 [55]. The heating rate varied between 2.3 and 9.3 minutes to reach 350 °C. It was found that although only a small amount of wood is converted below 300 °C, the degradation is complete by 330 °C.

When water:wood ratio was varied, the heat-up time was shorter for higher water content. In the experimental equipment used there was no liquid phase in the reactor above 175 °C to transfer heat at a water:wood ratio of 1. While the presence of liquid water appeared to have detrimental effects on initial conversion of wood to oil, it also provided beneficial effects by preventing char formation.

Smaller wood chips initially converted faster than large ones, but at the end of the heating period results were similar, and also similar to those obtained previously with powdered wood.

Later a 'cascade' reactor was constructed, allowing 100 g of chips to be processed at a time [56]. Since unusually high amounts of phenol had been obtained, the lignin was extracted from heartwood, sapwood and bark of different poplar clones. The amounts of phenol obtained varied, but the lignins gave consistent acetone-soluble oil yields of 75 % on aqueous thermal liquefaction, confirming the major contribution of the lignins to the oil.

A biomass liquefaction process being investigated at present is the HydroThermal Upgrading (HTU) process [53]. Autoclave experiments are carried out at Apeldoorn, to study phase equilibria and to provide input data for the design of a 20 kg/h pilot plant. Previous experiments at the former Shell Research technology centre in Amsterdam indicated that for the HTU process a ratio of water:dry matter of at least 3:1 is required. Very little information about the process is available in the open literature, but a thesis on hydrothermal conversion of carbohydrates and related compounds has been presented [57].

3.2.2.2 Flash pyrolysis processes

A number of flash pyrolysis processes are at present being developed [58]. The central features are the very rapid heating of biomass particles and the short residence time at about 500 °C to obtain the highest possible liquid yield. Fluid beds and circulating fluid beds are the most popular configurations due to their ease of operation and ready scale-up [59].

The flash pyrolysis process developed by the National Renewable Energy Laboratory (NREL), USA, utilizes a vortex ablative pyrolyser. Thus the process stream, recycled gas and feed, enters the vortex reactor tangentially, so that the particles are forced to the wall by large centrifugal forces. The particles slide and tumble on the reactor wall as they take a helical path through the reactor [60, 61].

Also the pyrolysis process developed by the Biomass Technology Group (BTG), The Netherlands, utilizes an unusual reactor configuration [62-64]. Biomass is intensely contacted with hot sand whereupon they both flow through the heated reactor. The reactor consists of the space between a rotating outer cone and a stationary inner cone.

The product 'oil' in all cases consists of a mixture of water, about 25 %, and liquids derived from the biomass, having an overall elemental analysis close to that of the original biomass. This oil is unstable, as well as corrosive. It may be used as fuel in intermediate size boilers, 100 kW to 1 MW, if combustion system components are modified and combustion chamber temperatures precisely controlled [65]. Emissions, though, especially of particulates, are higher than for medium light fuel oil. Flash pyrolysis oils may also be used for running diesel engines, after some modification, if 5 % diesel (by energy) is continuously added [66].

There is also considerable interest in upgrading of pyrolysis oils. Pyrolysis liquids from biomass are not miscible with, and bad co-feeds for, standard petroleum crudes and their fractions. At VEBA AG this upgrading was not found feasible since catalytic hydrotreating in fixed beds was not operable though it was possible in slurry phase reactors, but needed further confirmation. Costs were found to be much too high in comparison with conventional refinery streams [67]. At DMT, on the other hand, catalytic hydrogenation was found feasible, using the process configuration developed for hydrogenation of coal oil, though the high water content already in the input material was found to be a drawback [68].

Tests have also been conducted adding catalyst, ZSM-5 or a Y-zeolite, either with the raw material or directly into the flash pyrolysis reactor [69]. It was found that this changed the characteristics of the produced pyrolysis liquids, the most important change being the decreased viscosity. Long term effects and regeneration were not addressed.

In another study it was found that when HZSM-5 was used for vapour-phase upgrading of a bio-oil produced from oak sawdust, the catalyst contained 27 wt % coke after 30 minutes [70]. It was suggested that coke is formed by a thermally activated polycondensation of the largest compounds present in the pyrolytic vapours and that the zeolite external acidity does not play an active role in the deposition of this organic material. On the other hand, as usual in zeolite catalysis, a poisoning of the ZSM-5 internal acid sites was also detected.

In yet another study further steam was added to the pyrolysis vapours from wood and/or rice husks prior to upgrading [71]. ZSM-5 catalyst had been placed in the freeboard of a fluidized bed, to form a packed bed. The catalytic upgrading reduced the liquid yield considerably while the addition of steam diminished the decrease somewhat. The coke formation on the catalyst was decreased with the addition of steam.

There has also been interest in using flash pyrolysis products for the production of chemicals due to their much higher added value [72, 73].

3.2.3 Peat liquefaction

Extensive experience concerning especially liquefaction of coal has accumulated, as can be seen from the previous sections. Less work has been done on peat though studies on peat liquefaction were performed already by 1950 in Sweden [74-76].

If peat is liquefied, the liquid products can serve as raw material for synthetic liquid fuel production. The high moisture content in the natural deposits of peat, about 90 %, is the main obstacle to energy utilization of this fuel. Another obstacle is the high initial oxygen content in the organic matter of peat. The original idea of the 'Oil from Peat' project at KTH (1976-1991) was to simultaneously liquefy and dewater peat [77].

It was confirmed that the idea functioned in laboratory batch experiments [29, 77]. An organic product similar to very heavy oil was obtained after treating raw peat with CO at an initial pressure of 5.5-8.3 MPa and at temperatures in the range of 300-350 °C in the presence of K_2CO_3. This fraction spontaneously separated from the water phase. Calculations were made on elemental composition and amount of CO_2 evolved. The calculation showed that, despite the high initial oxygen content of the raw material, the product would consume less hydrogen than a bituminous coal in subsequent hydrotreatment.

Further studies were then conducted on the mildest conditions possible for obtaining phase separation between the hydrophobic product and the water phase [78, 79]. It was found that phase separation is favoured by more severe treatment conditions. The water phase, however, contains phenols and other oxygen-rich substances.

Using the water initially present in peat as a reaction medium has evident advantages, but also implies expensive high-pressure equipment and large amounts of waste water. An option could be deoxygenating raw peat and then using the deoxygenated product as input to a process resembling coal liquefaction.
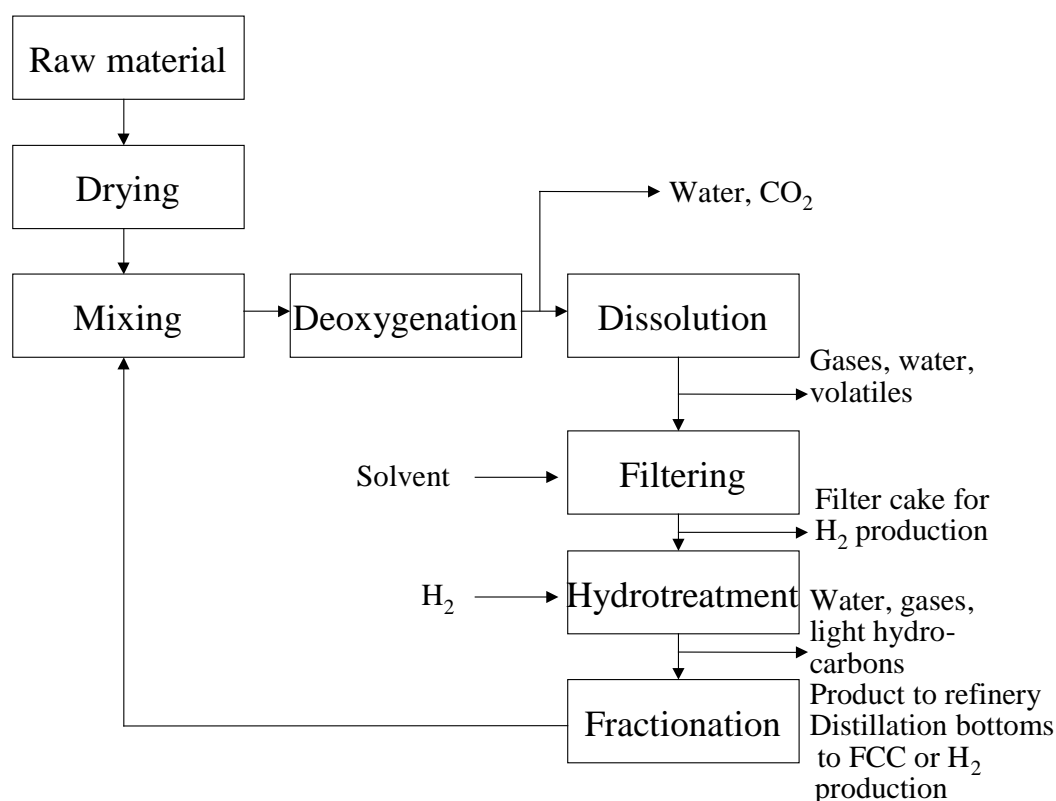

Figure 4 Schematic process scheme for liquefaction and primary hydrotreatment

Peat may after the deoxygenation step be supposed to be similar to coal [80]. Figure 4 shows a schematic diagram of liquefaction and primary hydrotreatment. Most important are the deoxygenation, dissolution and primary hydrotreatment steps.

Large amounts of CO_2 evolve when peat is thermally treated [79]. If gaseous hydrogen is used to supply the hydrogen necessary for stabilizing the formed radicals, it is diluted by the CO_2 evolved. Thus, in a process for peat liquefaction it is preferable to supply the needed hydrogen from a donating liquid, that is, if the amount necessary for achieving satisfactory dissolution can be made available. Another possibility is partial deoxygenation and liquefaction in a first stage without hydrogen, followed by a second stage at higher temperature with hydrogen.

When it is possible to produce a recirculating, raw material-based solvent with the desired properties, a great part of the work necessary for the development of a direct liquefaction process has been accomplished [81].

The function of the solvent is to transport the solid raw material through the process equipment and to transfer heat of reaction. The solvent must contain components that promote dissolution and inhibit the formation of condensed products. The composition of the solvent should also be such that the dissolved product remains in solution.

The activity and life-time of the hydrogenation catalyst depends on the composition of both the dissolved material and the recirculate. However, before producing a recirculating solvent, the prerequisites for obtaining a high degree of dissolution must be investigated.

3.2.4 Biomass gasification

Interest in the gasification of renewables arose from both the wish to improve efficiency in utilization of raw materials and the need for waste disposal [48].

Gasification studies were begun at Chemical Technology, KTH, already in 1974, then with the goal of producing methanol from peat or biomass. Research commenced with thermobalance studies of the reactivity of different raw materials, since basic kinetic data were found to be lacking [82]. Poplar wood and straw were found to be the most reactive in slow pyrolysis under argon; bark, a high moor peat and a low moor peat followed, these were all more reactive than coal. These studies led to the development, at Studsvik of the MINO (Minimum oxygen demand) pilot plant for production of synthesis gas for making methanol. Research focus at KTH shifted to basic problems in biomass gasification.

The advantages of gasification, compared to combustion, of a given raw material, are [43]:

1   Higher efficiency when electricity is produced by gasification followed by a gas turbine (so-called IGCC, integrated gasification combined-cycle) than when produced by combustion followed by a steam turbine (Rankine cycle).

2   The efficiency is also higher than for a conventional Rankine cycle when the gasification gas is combusted in an internal combustion engine.

3   Synthesis gas can be produced by gasification.

4   The gas volume after gasification is considerably smaller than after combustion, so, in some cases, there are possibilities for simpler and less expensive gas cleaning.

3.2.4.1 Main gasifier types

Unit size as well as how the gas is to be utilized affects choice of gasifier type, see Figure 5.

There are two main types of fixed bed gasifiers. Downdraft gasifiers are usually preferred for small-scale power generation since they give little tar. The downdraft gasifiers require uniformly sized input material of low moisture content. Several types are commercially available, but there are problems with the tar removal systems, usually wet scrubbing [83]. Downdraft gasifiers are especially difficult to scale up since they usually are narrower in the combustion zone; for diameters larger than 60 cm the distribution of fuel and gas becomes so uneven that the reactor does not function [43]. The devices used for producing the 'generator gas' that was used as automotive fuel during World War II are examples of downdraft gasifiers.

For small-scale heat applications several fixed-bed updraft (counter-current) gasifiers are commercially available, these have the advantages of accepting both moist and uneven-sized fuels, though the particles should not be too small to avoid large pressure drops. Updraft gasifiers give much tar but it contains mostly phenols and oxygenated compounds; polyaromatics, formed at high temperature, are caught on the way upward through the increasingly cool raw material. In downdraft gasifiers, on the other hand, only the most refractory tars survive since the air is contacted with the pyrolysis vapours when they are hottest.

Larger gasifiers are either bubbling fluidized beds or circulating fluidized beds. If the gas (air or other reaction medium) flow is sufficiently increased in an updraft bed, the particles begin to move about. When the pressure drop over the bed corresponds to the weight of the bed material, the bed becomes fluidized, it has become a bubbling fluidised bed. Fluidized beds normally require smaller particles than solid beds, but the particle size distribution can be larger than in fixed beds [43]. If gas velocity is increased further, large amounts of solids are entrained with the product gas, and a circulating fluidized bed (CFB) is obtained. The circulating
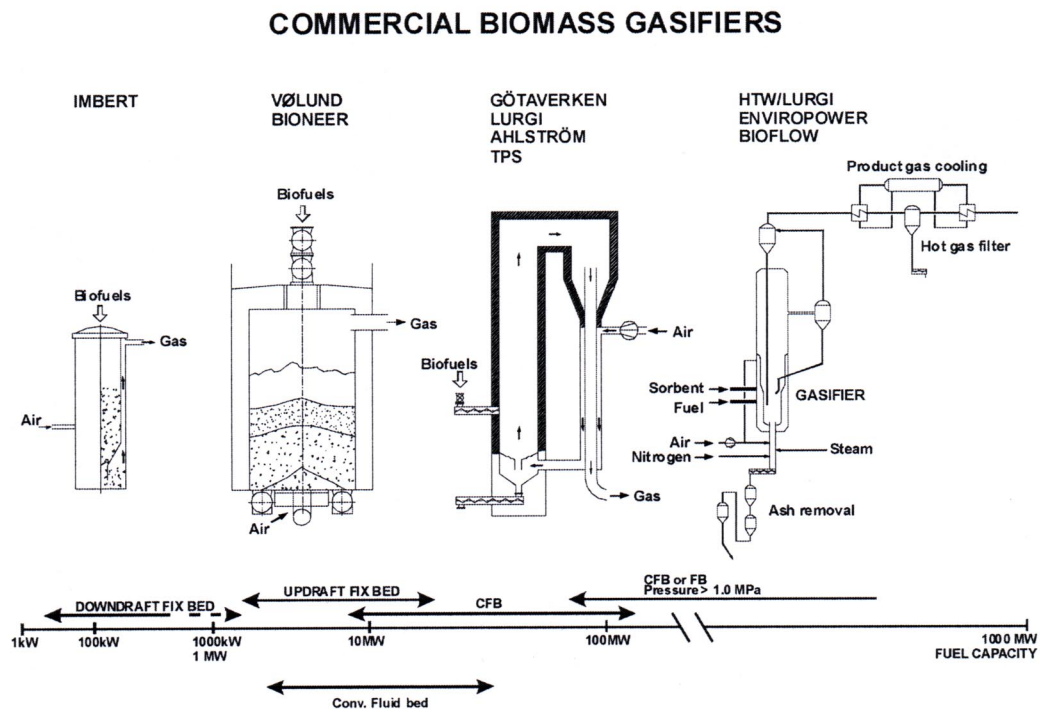
COMMERCIAL BIOMASS GASIFIERS

Figure 5 The four main types of gasifiers [84]

fluidized beds have the greatest throughput per unit area; entrained material is recycled back to the fluid bed to improve carbon conversion efficiency in comparison with the single fluid bed design.

3.2.4.2 Operating conditions

Biomass gasifiers are usually run in the temperature interval 800-950 °C. The lower temperature limit is set by tar formation and carbon turnover while the higher temperature limit is set by ash sintering. Generally, the ash softening temperature decreases with increasing silica content in ash. It should be noted that ash fusion tests do not always predict behaviour in a gasifier [20]. For example, the ash of reed canary grass is Si-rich; in spite of this the initial ash deformation temperature is above 1440 °C while the sintering temperature lies in the interval 800-900 °C.

Also high alkali contents cause corrosion and sintering problems.

The tar produced in fluidized bed gasification can be considered a blend of the two types produced by downdraft and updraft fixed bed gasification, respectively. A high freeboard above the gasifying bed, in a bubbling fluidized bed, gives the tar a relatively long residence time at high temperature, allowing time for thermal cracking.

An inert material is usually present in fluidized beds. This inert bed improves fluidization characteristics and heat transfer. The most common bed materials are dolomite and magnesite [43].

If the product gas is to be used in pressurized equipment, the gasifier itself is usually pressurized though this entails more complex and costly feeding and higher capital costs. Efficiency, however, is increased. Hot gas cleaning is usually used in pressurized systems, this reduces thermal and pressure energy losses and is in principle simpler and of lower cost than scrubbing systems.

Air gasification produces a poor-quality gas in terms of heating value (4-7 MJ/m_n^3 higher heating value) which is suitable for boiler, engine and turbine operation, but not for pipeline transportation due to its low energy density. Oxygen gasification produces a better-quality gas (10-18 MJ/m_n^3 higher heating value) that is suitable for conversion, for example, to methanol and gasoline [85].

3.2.4.3 Operational and projected advanced systems

Probably the only biomass gasifier for synthesis gas production that has operated commercially used peat as raw material. It was located at Oulu in Finland, where at the end of the 80's 25 tonnes peat/h were gasified at 10 bar with oxygen to yield synthesis gas for ammonia production. During the several thousands of hours operating experience, many technical problems were encountered and subsequently solved. At the end, it could be concluded that the technology was technically proven [83].

Several circulating fluidized beds using biomass as raw material are in commercial operation, they use wood wastes to fire lime kilns at capacities ranging from 15 to 35 MWt [83].

A 15 MW CFB for refuse-derived fuel (RDF) was built in Grève-in-Chianti in 1991, the product gas to be used in a cement kiln or in a purposely designed steam boiler for power generation [86]. A second CFB was later built, 3.3 MWe was produced in the turbine [87].

It is planned that the European Union will implement a Directive on incineration of wastes in 2002; no deposition of combustible refuse will henceforth be allowed (with a relatively long transition period) [88]. The requirements on operating conditions, emission limit values and monitoring are together quite severe. Many existing waste treatment facilities will have to be modified, and many more have to be built [89]. The use of RDF as raw material for gasification entails special difficulties as to chlorine content and heavy metals, but is one of the options for complying with the requirements.

Some of the more advanced projects utilizing biomass gasification are shortly described below.

A pressurized CFB is at the centre of the first biomass-based IGCC plant to be built and operated. It is located at Värnamo, Sweden, and has the capacity to produce 6MWe and 9 MWt [90]. It is now in mothballs after the completion of the intended demonstration programme.

The test runs were designed to allow an overall assessment of plant performance. Other tasks were to propose modifications of components and systems in future plants and to evaluate operating costs for an assessment of technical and economical possibilites for the technology.

An interesting result of the demonstration programme is the high fuel flexibility. Bark turned out to be the fuel that worked best in the gasifier and adjacent systems. Since bark, more 'difficult' than wood chips and wood residues, worked well, also *Salix* was tried and worked well. This was also the case for straw; agglomerates were formed but these were rapidly separated from the bottom ashes before they were returned to the (magnesite) bed. Even RDF could be used as raw material, but not alone since it contains so much ash that there was not enough capacity in the fly ash system.

No thermal NO_x was formed in the gas turbine. Fuel NO_x was, however, formed, the amount depending on nitrogen content in the raw material. Since straw contains much chlorine, the emissions when running the plant on straw were tested for their dioxin content. The dioxin content was found to be 0.01 ng/Nm^3, one tenth of the proposed allowable concentration in emissions from RDF-fuelled plants within the EU.

The Thermie programme of the European Union has specially supported several projects for production heat and electricity from gasified biomass [83]. One of these projects is the ARBRE (ARable Biomass Renewable Energy) facility at Aire Valley in Yorkshire which is intended to begin operating in the spring of 2001. It is to deliver 8 MWe to the grid, the input material will mainly be a mixture of dedicated *Salix* and poplar clones, fertilized by sewage sludge. The gasifier is a TPS (Termiska Processer AB, Studsvik) circulating fluidized bed. The tars will be cracked at 900 °C in a second circulating fluidized bed utilizing dolomite as bed material. The gas is then cooled to about 40 °C, before being compressed. The gas then enters a conventional gas turbine.

An atmospheric TPS CFB gasifier is also intended to be used in a Brazilian facility in Bahia, to be funded by the World Bank.

3.2.4.4 Fundamental problems in gasification

To optimize a process, a better understanding of the fundamentals is needed. Some of the fundamental problems in gasification have been intensively studied within the Gasification group at Chemical Technology.

Char gasification is the slowest step in the gasification process. A semi-empirical gasification kinetic model has been developed [10]. Different rate equations are used for coal, lignite and peat, on the one hand, and most types of biomass, on the other hand, depending on whether reactivity decreases or increases with increasing time or conversion. The time-temperature-environment history of char formation also exerts a substantial effect on its reactivity [91].

It has been found that the feeding point in an atmospheric fluidized bed influences fuel-nitrogen conversion to NH_3 and with that NO_x formation in subsequent combustion [92]. Experiments in fluidized beds have shown that NO can be present in substantial concentrations in the bottom section of the fluidized bed and that a high content of CO in a gasifier strongly promotes NO reacting with the char. The reaction between NO and char into N_2 is possibly important in explaining the difference in NH_3 conversion for top and bottom feeding.

Tar is defined, according to the International Energy Agency's preliminary tar protocol, as organic components/contaminants with a molecular weight greater than that of benzene [93]. Tar is usually only a small percentage of the product gases but it contains a proportionally large share of the heating value. When producer gas is used for thermal applications, there may be no need for tar cleaning since tar burns well with smokeless flame, but there may still be condensation problems in transfer lines. However, if the produced gas is to be used for shaft power production in internal combustion engines, tar concentration should not exceed 10 mg/m_n^3 [94]. A sampling method based on solid-phase adsorption (SPA) on amino phase has been developed within the project. The advantages include sampling speed, simplicity, less solvent consumption, faster work-up, accuracy and repeatability. However, this method is so far only applicable to light tar compounds up to a molecular weight of 300 g/mol (coronene) [95].

4 OVERVIEW OF PEAT LIQUEFACTION RESULTS (I)

This paper summarizes much of the work performed within the 'Oil from Peat' project at KTH.

There are two major problems with the utilization of peat for energy purposes: the large moisture content in the natural deposits and the high oxygen content in the organic material.

Initial research on peat liquefaction at KTH focused on simultaneous dewatering and liquefaction. The idea of using CO in coal liquefaction, revived in the United States after World War II, provided an attractive approach for the liquefaction of peat. The raw peat could be treated with CO and the water initially present could serve as reaction medium; additional solvent would be avoided, and the CO would be a source of H_2 via the shift reaction.

It was found, in co-operation with a Canadian group working on dry peat liquefaction with the addition of CO and H_2O, that raw peat with 90 % moisture treated with CO under high temperature and pressure gave a product similar to heavy oil [77]. Phase separation of this product and the water was obtained after the reaction.

The original idea was to develop a process resembling a coal liquefaction process. While there are evident advantages of using the water initially present in the peat as a reaction medium, it implies high-pressure equipment and large amounts of waste-water. An option could be partial dewatering and deoxygenation of raw peat and then using the deoxygenated product as input to a process resembling coal liquefaction.

A continuous unit for the liquefaction of raw peat was built during 1980-1984, see Figure 6. A high pressure feeder for solids, not shown in the figure, was also constructed. It can feed peat or biomass against a pressure of 30 MPa. The continuous unit operated satisfactorily during the first experiments, but was then shut down due to lack of funding.

The high oxygen content in peat, compared to coal, does not justify the assumption that peat would consume more external hydrogen than coal when converted into liquid fuels. It is the hydrogen content in the deoxygenated material which determines the amount of hydrogen required for further hydrotreatment, *i.e.* $(H - 2 \times O)/C_{atomic}$.

Experiments on deoxygenation under CO of various raw materials have been conducted. Temperature has the most pronounced effect on the formation of products in peat liquefaction. For highly humified peat, formation of a toluene-soluble fraction is favoured both by increased CO pressure and increased temperature. Simultaneously the toluene-insoluble fraction decreases. However, the
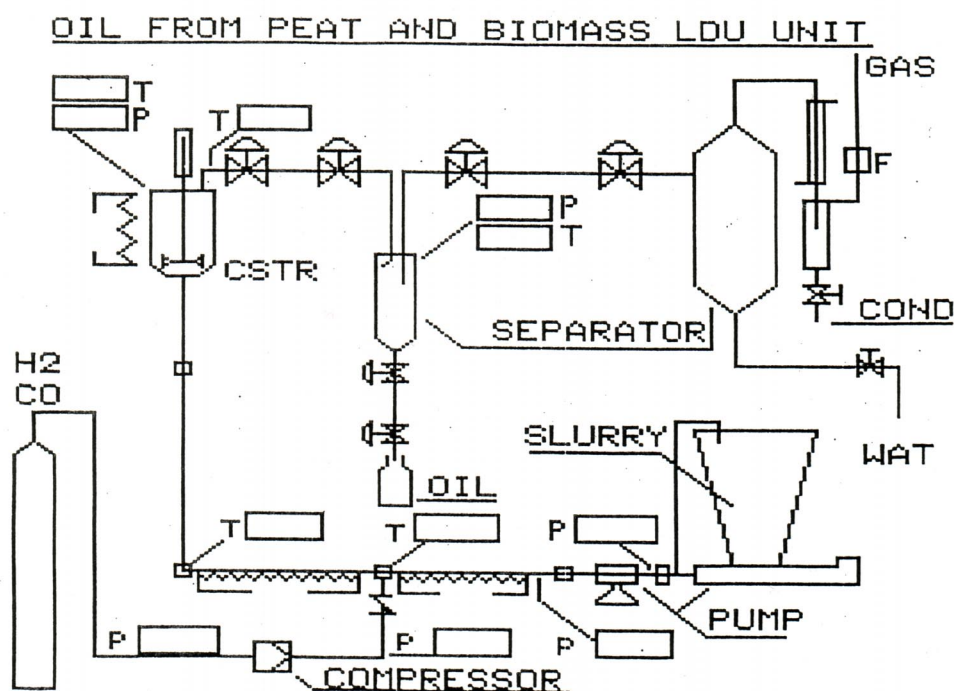
Figure 6 Continuous unit for high-pressure liquefaction of peat and biomass

sum of toluene solubles plus toluene insolubles increases somewhat with increased CO pressure and temperature, *i.e.* the sum of losses, as water, water solubles and gases, decreases.

Also for peat with a higher oxygen content the amount of toluene solubles increases while the amount of toluene insolubles decreases with increased CO pressure and temperature. But, for this raw material the sum of the two decreases with increasing severity of parameters.

Thus, for the peat with the high oxygen content, the reactions leading to formation of water-soluble compounds would seem to dominate. For the more decomposed peat, it would seem that stabilization of the formed radicals with formation of organic solvent-soluble and insoluble products dominates.

The elimination of oxygen-rich compounds in the first stage of peat liquefaction results in the formation of residual material with low oxygen and high energy content. Large material losses are not accompanied by proportionate energy losses.

The work on organic and simulated recycle solvents is discussed in the summaries of Papers II and III.

Because the chemistry of the process is so important, the development of analytical methods for the liquid products had a key role in the project. This later resulted in a PhD thesis on the development of methods using liquid chromatography and infrared spectroscopy for the characterization of peat liquids [96].

5 COMPARISON OF PEAT, BIOMASS AND COAL DISSOLUTION IN TETRALIN (II)

The degrees of dissolution of coal, peat, wood and cellulose in tetralin were compared. The objective was to obtain information about the differences between coal dissolution on the one hand, and dissolution of peat and wood on the other hand. This to increase understanding of how a coal liquefaction process should be modified to allow use of other input materials.

Tetralin (1,2,3,4-tetrahydronaphthalene) is a model compound for hydroaromatic structures in coal, widely used as a hydrogen-donor solvent in coal liquefaction experiments. Up to a temperature of 400 °C the thermal dissociation of pure tetralin is very slow, not reaching more than a few percent after 8 hours [97]. Up to the same temperature the formation of naphthalene well corresponds to the conversion of tetralin in the presence of coal [98].

The raw material was dried at 50 °C under CO_2/vacuum. Thereafter it was ground in a Retsch ultracentrifuge under a stream of CO_2. With a sieve with holes of 0.12 mm a stirrable slurry was obtained with a 1:3 ratio of raw material to tetralin. Approximately 130 g raw material and 390 g tetralin was used in the experiments. The heating up time for the experiments varied between 121 and 160 minutes, mainly depending on the chosen reaction temperature. During heating and cooling the slurry was stirred by a propeller at 1000 rpm, during the time at the reaction temperature rotation speed was 1500 rpm.

For coal, the dissolution at 350 °C is very low and independent of the processing time in the interval 15 to 120 minutes. Coal conversion at 445 °C, however, is considerable after 15 minutes. Longer processing times have no effect on coal dissolution but tetralin consumption increases considerably.

Peat dissolves in tetralin already at 350 °C and the conversion depends both on the temperature and the duration of the process. The influence of the reaction time decreases with the increase of temperature. The consumption of tetralin increases with time and temperature.

Biomass and cellulose dissolution in tetralin is considerable at 350 °C and 15 minutes processing time. The conversion of the solid material increases with increased temperature and time. Higher processing temperature and longer duration contribute mainly to the consumption of the hydrogen donor solvent.

Figure 7 shows conversion of the different raw materials as function of temperature, after 15 minutes. It may be seen that peat and biomass are much more reactive than coal. The difference is very significant at lower temperatures. Peat and biomass can be dissolved in tetralin already at 350 °C. Approximately 80 % of these raw materials are converted at 375 °C. The same conversion of coal can be
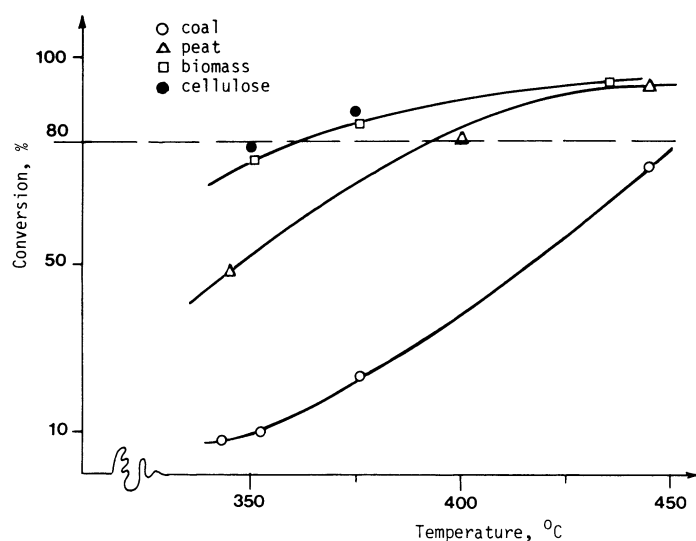
Figure 7 Conversion of coal, peat, biomass and cellulose after 15 min thermal dissolution in tetralin

reached at a temperature of 450 °C. Coal is practically not dissolved in tetralin at 350 °C.

Figure 8 shows the conversion of tetralin into naphthalene in the presence of different raw materials for the same processing conditions as in Figure 7. The
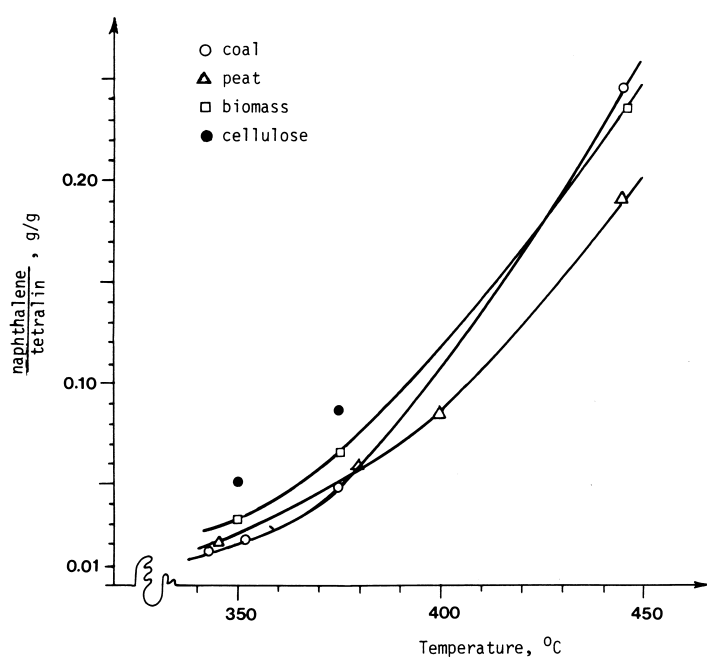

Figure 8 Consumption of hydrogen-donor solvent, tetralin, in thermal dissolution of coal, peat, biomass and cellulose after 15 minutes holding time

42

consumption of hydrogen from the different raw materials is nearly equal though coal conversion is much lower.

The consumption of hydrogen from the hydrogen-donor solvent is worth further discussion. Figure 9 shows the transformation of tetralin into naphthalene as a function of the conversion of the different fuels. The curve obtained for coal differs markedly from those obtained for peat, biomass and cellulose. The conversion of coal and the consumption of hydrogen begin simultaneously. The consumption of tetralin for the younger fuels is lower and begins only after the conversion of the solid fuel has advanced considerably. The initial conversion stages of the younger fuels seemingly consist mainly of thermal decomposition with evolution of H_2O and CO_2. The further dissolution of the younger raw materials is similar to that of coal and occurs with participation of hydrogen from the solvent. Peat has a somewhat intermediate position between coal and biomass. The consumption of of tetralin in the presence of coal is much higher, hovever, than that observed in the presence of peat and biomass. Thus, the higher the initial oxygen content of the solid fuel, the longer is the initial conversion period in which no hydrogen consumption from the hydrogen-donor solvent occurs.

The observed phenomenon is of considerable practical importance. It indicates that the hydrogen consumption (using H-donor) in the liquefaction processes of the younger fuels is not as high as expected, considering their high oxygen content. Table 7 shows the amount of CO_2 evolved in percent of dry ash-free input material for the different raw materials at 350 °C. It can be seen that the amount of gas obtained from coal is very low, while peat, biomass and cellulose evolve large quantities of CO_2. A considerable part of the O content of these young fuels is removed by thermal decomposition of the fuel with CO_2 evolution.
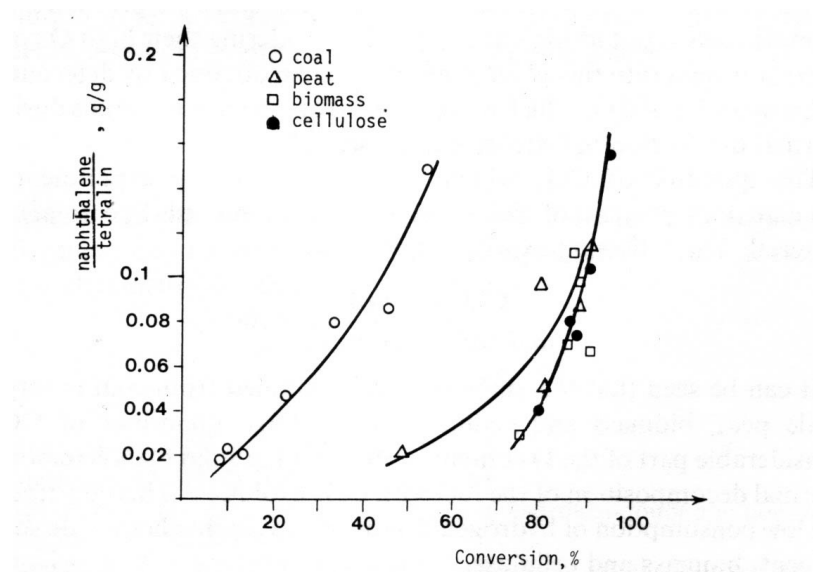

Figure 9 Consumption of tetralin as a function of solid fuel conversion

Table 7 Evolution of CO_2 in thermal dissolution in tetralin of coal, peat, biomass and cellulose

Raw material	Exp. no.	Processing time (min)	Temperature (°C)	CO_2 evolved*
Coal	K4	120	343	0.4
Peat	T7	15	350	18.3
Biomass	B2	15	345	16
Cellulose	C3	15	350	15.4

* in % of dry-ash free raw material

6 PEAT DISSOLUTION IN SIMULATED RECYCLE SOLVENTS (III)

The experimental series reported was undertaken to study whether, for practical purposes sufficient dissolution of dried peat could be obtained in a simulated recycle solvent under conditions resembling those used for coal liquefaction.

We also wanted to study the influence of variations in solvent composition on peat dissolution. The properties of the simulated recycle solvents were to be based on those obtained for a hydrotreated peat-derived liquid product. Thus, the simulated recycle solvent proposed by Whitehurst *et al.* [42] for coal had to be modified to formulate the composition of the solvent for the central point in a factorial design.

Preliminary recirculation experiments were made. Peat was dissolved in tar at 300/420 °C and the filtered product was diluted with o-xylene and hydrotreated at 350 °C. The product of this hydrotreatment plus some further o-xylene was used as solvent for fresh dried peat. The filtered product vas again hydrotreated. Elemental and n.m.r. analysis showed that a product with (by weight), 2 % oxygen, 1 % donatable hydrogen and 44 % aromatic carbon is attainable for a hydrotreated peat liquid.

A 2^3 factor experiment was designed around these values with tetralin as hydrogen-donor and naphthalene as additional aromatic solvent, considered to have hydrogen-shuttling ability. P-cresol is considered to have good physical dissolving properties, besides supplying the oxygen needed to simulate the peat-derived liquid product; p-cresol is also aromatic. Dodecane was used as a diluent to make the total weight of the solvents constant. The ratio of dried peat to solvent was chosen to give a small margin to the 1:2 ratio that earlier had been found possible to mix at room temperature. The amounts of peat and solvent components are given in Table 8. Dissolution experiments were conducted at 420 °C for 15 minutes.

An aim for the analysis of experimental results was to find an expression for the amount of solid residue as a function of solvent composition. To reduce experimental error, the amounts of tetralin, naphthalene and p-cresol in each solvent were divided by the amount of ingoing dry and ash-free (daf) peat. These amounts were normalized in accordance with usual statistical procedure [99]. However, it was found that, instead of using the amounts of the individual aromatic solvent components, total aromaticity of solvent could be used (*i.e.* g tetralin $\times$ 0.545 + g naphthalene $\times$ 0.938 + g p-cresol $\times$0.667). It was found that the amount of solid residue depends only on the tetralin and the total amount of aromatic carbon present in the solvent. The best fit between experimental results and solvent composition was found for the following equation:

$$\% \text{ Solid residue (daf)} = 32.85 - 7.71 \times \ln(x_1) - 12.42\, x_4 \qquad (1)$$

Table 8 Amounts of peat and solvent components in dissolution experiments

Exp.	Dry peat (g)	Solvent (g)	Tetralin (g)	Naphthalene (g)	p-Cresol (g)	Dodecane (g)
1-1	31.01	72.28	8.79	5.02	3.76	54.70
1-2	30.73	71.64	8.72	4.99	3.75	54.18
2-1	30.83	71.74	32.45	4.99	3.74	30.56
3-1	31.94	72.20	8.80	17.60	3.77	42.05
4-1	31.25	73.28	32.72	17.63	3.78	18.25
5-1	30.89	72.01	8.77	4.98	13.78	44.47
5-2	31.17	72.00	8.77	4.98	13.78	44.47
6-2	31.94	72.04	32.56	5.01	13.83	20.65
7-1	30.96	71.72	8.74	17.43	13.72	31.84
8-2	30.89	71.90	32.52	17.50	13.74	8.13
C 11	30.81	72.60	20.85	11.36	8.83	31.55
C 12	31.09	71.94	20.66	11.25	8.75	31.27
D 1	30.89	71.99				71.99
D 2	31.12	72.12				72.12

where x_1 is the ratio of tetralin in the solvent to peat (daf) and x_4 is the ratio of the total amount of aromatic carbon in the solvent to ingoing peat. Thus total aromaticity of solvent might be considered a practical unit. However, it is probably not transferable to a simulated recycle solvent with other aromatic components.

Peat is not a homogeneous raw material, just as coal is not. Thus, the results obtained in this experimental series may not be applicable to a peat with another composition or botanical origin (see below, section 6.1).

As can be seen in Figure 10, increased aromaticity increases dissolution at a given concentration of hydrogen donor. However, it seems that a high degree of dissolution cannot be obtained without considerable hydrogen donation.

In Figure 11 the amounts of hydrogen donated are plotted against the total aromatic carbon of the solvents. It can be seen that to achieve effective use of the potentially available hydrogen for peat dissolution, the solvent has to have physical dissolving ability. The solvents seem to have different maxima for hydrogen donation depending on initial tetralin content. Thus, when more hydrogen is available for donation, the maximum is reached for a more aromatic solvent. For both low and high initial tetralin content in solvents there is a decrease in net donated hydrogen above a certain aromaticity of the solvents. An explanation may be that when the solvent has enough physical dissolving and shuttling ability, *i.e.* is aromatic enough, the peat itself supplies some of the needed hydrogen, and at a greater rate than tetralin.
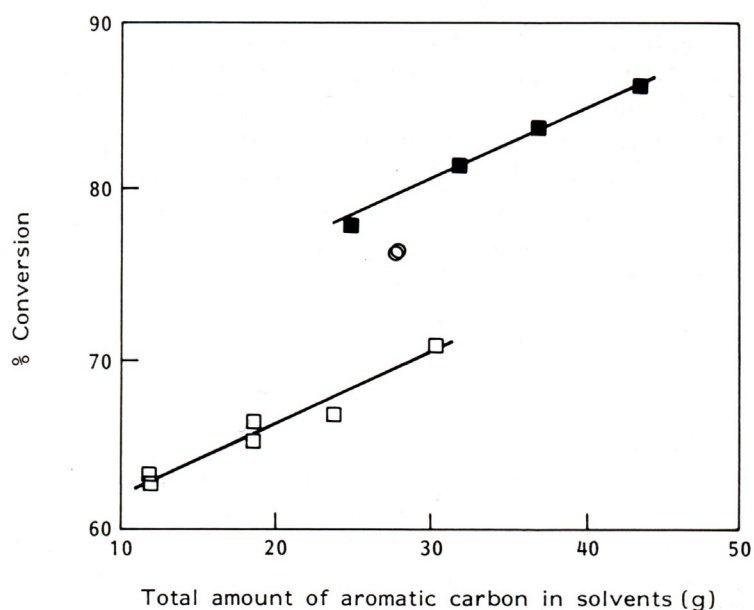
Figure 10 Conversion as a function of total aromaticity of solvent at the different levels of initial tetralin concentration in solvents: □, low; ■, high; ○, centre. The solid lines are calculated using equation (1)

It is doubtful whether the degree of dissolution achieved in the experiment with the highest dissolution is large enough for a process for peat liquefaction. Though the
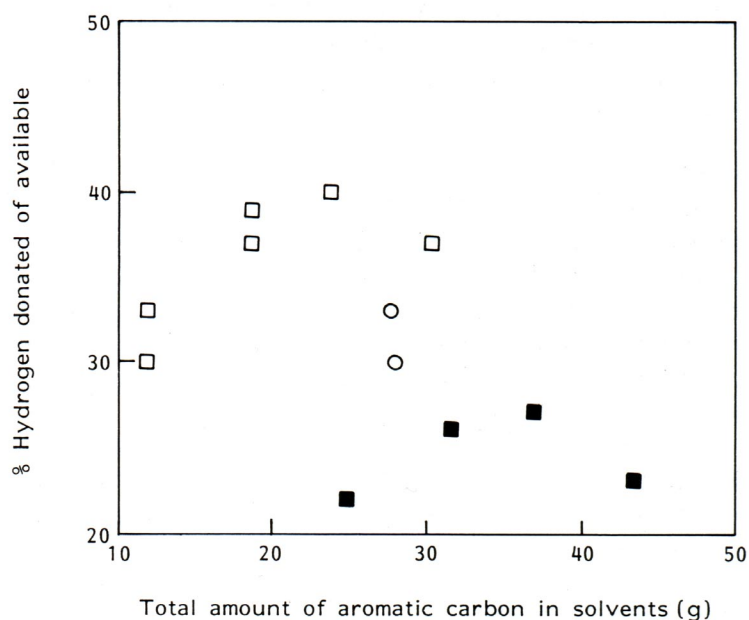

Figure 11 Percent hydrogen of available donated from tetralin as a function of total solvent aromaticity at the different levels of initial tetralin content in solvents: □, low; ■, high; ○, centre

amount of solid residue is only 14 % (daf) of ingoing peat (daf), it contains slightly above 20 % of the energy in the dried raw material. This is probably in excess of what is needed for the production of energy and gas required for a process.

The amount of donatable hydrogen may probably not be increased by further hydrogenation of the process-derived solvent if it contains only 44 % aromatic carbon, as was the case for the hydrotreated peat-derived liquid which formed the basis for this experimental series. Further hydrogenation may instead lead to saturation, less donatable hydrogen and deteriorated dissolving properties. However, analysis of the high-boiling fractions of experiments 6 and 8 of this experimental series indicates that aromaticity of dissolved product increases with degree of dissolution. This may represent a possibility for obtaining a peat-derived recycle solvent with a higher percentage of donatable hydrogen.

6.1 Dissolution of a peat with high heating value

The peat used for the experiments in Paper III came from Skråttmyran. In a later, unpublished, experimental series with simulated recycle solvents, another peat, Nb 22, was used. The elemental analysis of both peats is given in Table 9. The Skråttmyran peat is representative of peats harvested in central Sweden, while Nb 22 is unusual. It has a high heating value and should be a good raw material for liquefaction [35, 79]. It was kindly provided by a peat characterization project at The Swedish University of Agricultural Sciences, Umeå. It was chosen because it deviated the most from the other samples in the multivariate analysis of properties of collected peat samples made [100].

The study using Nb 22 as raw material was undertaken to see whether the same type of correlation that was obtained for the Skråttmyran peat could be applied to another type of peat.

6.1.1 Apparatus and procedure

Experiments with peat Nb 22 were made in the same manner as with the Skråttmyran peat, using a 250 ml autoclave with a magnetic stirrer. Time at 420 °C was 15 minutes.

The experimental series for Skråttmyran peat was made in a strictly factorial design, but for Nb 22 solvent composition was varied more, to test the limits of acceptability. The composition of the reactor inputs for Nb 22 and the percentages solid residue are given in Table 10.

Workup procedure for experiments with Nb 22 was simplified since interest was focused on the degree of dissolution. Reactor contents were washed out with a mixture of toluene/ethanol and filtered in the same way as for the Skråttmyran peat.

Table 9 Elementary analyses, in wt %, of dry peats used in simulated recycle solvent runs

	C	H	N	O (by diff)	Ash
Skråttmyran	51.6	5.8	2.0	35.6	5.0
Nb 22	60.6	6.1	2.6	24.8	5.9

6.1.2 Results and discussion

All of the experiments in the series with peat Nb 22 could not be made to fit regression analysis satisfactorily. For both experiments 6 and 7, the ratio of total aromaticity and hydrogen-donating power to input peat was also much higher. The lesser degree of filling of the reactor in experiment 7 may also have influenced results in an unpredictable way.

Excepting experiments 6 and 7, conversion for Nb 22 in simulated recycle solvents could satisfactorily be expressed by the same type of correlation as found for the peat from Skråttmyran, *i.e.*:

$$\% \text{ Solid residue (daf)} = A - B \times \ln(x_1) - C\, x_4$$

where x_1 is the ratio of tetralin in the solvent to peat (daf) and x_4 is the ratio of the total amount of aromatic carbon in the solvent to ingoing peat. The values for the two peats are then:

	A	B	C
Skråttmyran	32.85	7.71	12.42
Nb 22	33.02	10.93	9.19

Nb 22 is more difficult to dissolve than the peat from Skråttmyran. It would seem that Nb is more dependent on solvent hydrogen-donating power than the Skråttmyran peat. Also, for Nb 22 the aromaticity of the solvent seems less important.

Achieving a satisfactory dissolution, if it is assumed to be about 10 % solid residue, would seem to be impossible within the experimental range studied. A solvent consisting of only 72 g tetralin (to 31 g peat daf) would have a ratio of tetralin/peat of 2.3, which falls outside the studied experimental range; the aromaticity of this solvent (g aromatic carbon/g peat) would, however, be inside the range, with the value 1.27. The theoretical amount of solid residue would then be 10.6 % for the Skråttmyran peat while it would be 12.1 % for the Nb 22 peat.

Table 10 Amounts of peat, solvent components and amounts of solid residue in dissolution experiments with peat Nb 22

Exp.	Dry peat (g)	Solvent (g)	Tetralin (g)	Naphthalene (g)	p-Cresol (g)	Dodecane (g)	Solid residue (%)*
C-2	32.53	72.15	20.71	11.29	8.78	31.37	28.5
4-3	31.55	71.68	32.32	17.48	3.80	18.08	21.6
3	31.84	72.21	44.54	17.64	3.76	6.27	15.8
4	31.83	71.37	44.07	4.94	3.72	18.64	19.8
5	31.57	71.84	56.68	5.12	3.75	6.29	14.5
6	25.11	78.23	34.57	35.99	2.94	4.73	15.0
4-4	31.87	72.25	32.58	17.62	3.83	18.22	20.3
7	21.46	71.74	44.25	17.52	3.74	6.23	15.2
D3	31.80	72.34				72.34	43.0

* dry ash-free solid residue of dry ash-free input peat

The results indicate that for a peat with a comparatively high heating value, parameters more closely resembling those for coal liquefaction must be used. The recycle solvent must have greater hydrogen-donating capacity to obtain a satisfactory dissolution.

7 TAR DECOMPOSITION OVER DOLOMITE AND SILICA (IV)

In this study the catalytic effect of dolomite and silica, two widely available and inexpensive materials, on the decomposition of some biomass tars was investigated.

Generally, it is easier in lab scale to pyrolyse than to gasify biomass to obtain a tar-rich gas that can be used as input for tar decomposition studies. Since pyrolysis gives a more tar-rich gas than gasification, it was assumed appropriate to use a pyrolysis gas to study the decomposition of tar although compounds and proportions are somewhat different. The experimental equipment includes two reactors, the pyrolyser and the fixed-bed catalytic cracking reactor. A rotating conveyor gradually introduces the raw material at a controlled rate into the heated pyrolyser. A carrier gas is used to transport the tar-rich gas produced in the pyrolysis unit through the catalytic reactor.

Tar decomposition has been extensively studied. The cracking effect of inexpensive materials such as dolomite and CaO on the decomposition of both real tars and model compounds has been demonstrated. Tar may also be decomposed using nickel-based catalysts, but these are more expensive. In some instances, dolomite has been used as guard bed before nickel catalysts [101-103].

Naphthalene is one of the most stable tar compounds and it is difficult to eliminate by catalytic decomposition. Even small amounts of remaining naphthalene will condense and cause problems in downstream equipment. When dolomite is used as catalyst, naphthalene is almost the only compound left, besides benzene. Benzene is not a problem, though, since it stays in the gas phase.

The idea of using silica for tar decomposition came from rice husk gasification experiments in India [104]. Rice husk ash consists almost only of silica and tar from gasification of rice husk has previously been found to contain unusually low amounts of naphthalene compared to tars from gasification of other raw materials. Rice straw only contains about 5.5 % lignin [105] while rice husks contain 26 % Klason lignin [106]. The absence of tar-forming lignin could thus not be the cause for the observed low amount of tar. A commercial silica catalyst was used in the experiments.

The yield and the composition of the tar depend on the raw material. The differences decrease with increasing temperature in the cracking reactor. In the thermal cracking experiments three different raw materials, birch, *Miscanthus* and straw, were characterized for their light aromatic compounds using the SPA method at three different temperatures. The results are shown in Table 11.

Main components in the analysed samples in Table 11 are benzene, toluene and naphthalene. The amounts of benzene and naphthalene increase with temperature,

Table 11 Individual light tar compounds and benzene (in mg/g dry raw material) from birch, *Miscanthus* and straw after thermal cracking at 700, 850 and 900 °C

Feedstock	Birch			*Miscanthus*			Straw		
Temperature (°C)	700	850	900	700	850	900	700	850	900
Benzene	0.6	1.1	2.4	3.3	3.1	5.4	0.7	0.8	0.9
Toluene	1.5	1.5	1.7	3.2	2.7	2.2	1.1	1.1	0.7
p-Xylene	0.6	0.4	0.1	0.6	0.4	0.2	0.4	0.2	0.1
o-Xylene	1.2	1.2	0.7	1.5	1.2	0.7	1.3	1.0	0.6
Indene	0	0.1	0	1.3	1.4	0.6	0.2	1.0	0.4
Naphthalene	1.0	2.5	2.3	1.6	3.3	3.7	2.2	3.3	3.9
2-Methylnaphthalene	0.1	0	0	0.5	0.5	0.3	0.3	0.3	0.1
1-Methylnaphthalene	0.1	0	0	0.1	0.2	0.1	0.3	0.2	0.1
Biphenyl	0	0	0	0	0.1	0.1	0.2	0.2	0.1
Acenaphthylene	0	0	0	0.4	0.8	0.6	0.5	0.5	0.5
Fluorene	0.1	0	0	0	0	0	0.1	0.2	0.2
Phenanthrene	0	0	0	0.2	0.5	0.5	0.3	0.3	0.6
Anthracene	0	0.3	0.3	0.1	0.2	0.2	0.1	0.1	0.2
Fluoranthene	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
Pyrene	0	0	0	0	0.1	0.1	0.1	0.1	0.3
Total light aromatics excluding benzene	4.6	6.1	5.2	9.6	11.5	9.4	7.2	8.6	8.0

while other light tar compounds up to 1-methylnaphthalene decrease. It may be seen that thermally cracked birch has the lowest indene and naphthalene concentrations.

Tars from birch and *Miscanthus* have also been characterized after decomposition over dolomite. Table 12 shows benzene and some light key compounds in tar from

Table 12 Benzene and some key aromatic components in tar (in mg/g dry raw material) after catalytic decomposition of birch and *Miscanthus* over 30 g dolomite at 850 and 900 °C

Feedstock	Birch		*Miscanthus*	
Temperature (°C)	850	900	850	900
Benzene	2.8	7.3	8.6	16.1
Toluene	2.1	1.3	3.6	2.7
Indene	0.06	0.03	0.02	0.02
Naphthalene	2.4	1.6	2.6	3.4
Total light aromatics excluding benzene	7.1	4.4	7.5	6.8

these experiments. The higher concentration of some tar compounds at 900 than at 850 °C, especially for *Miscanthus*, is due to the fact that these compounds are products in the decomposition of heavier tar compounds.

When tar concentrations after thermal cracking, Table 11, are compared with tar after catalytic decomposition, Table 12, the larger absolute numbers in Table 12 should not lead to the conclusion that there is a higher amount of tar after catalytic cracking than after thermal cracking. The SPA method only analyses light tar components and catalytic decomposition increases the portion of these components in total tar.

From previous experiments it is known that after catalytic decomposition at 900 °C the amount of heavy tar compounds are negligible and they constitute only a few percent of total tar at 850 °C [107]. Phenols and aromatic nitrogen compounds have previously also been analysed but their amounts constitute only an insignificant portion of the total tar for the used conditions. The presence of notable amounts of phenols indicate the presence also of heavy tar [108].

To improve the performance of dolomite as tar decomposition catalyst, especially for the decomposition of naphthalene, dolomite was tested in different combinations with silica (D11-11 from BASF).

The concentrations, after tar decomposition, of naphthalene and total light aromatics from these experiments are shown in Table 13 for birch and *Miscanthus*. It may be seen that dolomite and silica, used alone in equal amounts have practically the same activity for decomposition of the total light aromatics and naphthalene. A further decrease of the amounts of total light aromatics and naphthalene was obtained using mixtures of both catalysts in large amounts. Dolomite alone used in the same large amount seems to be more efficient. When silica and dolomite are combined in two separate layers with silica on top (the tar-rich gas passes first over silica and then over dolomite) the outcome is noteworthy. Naphthalene and total tar amounts are now smaller than for the corresponding amount of mixed catalysts or for the same amount of dolomite alone.

The temperature in the cracker during the experiment with the layered catalyst on tar from birch was too high though, by about 20-25 °C. When the experiment was repeated, another silica catalyst was used (BASF D11-10) and this catalyst gave larger amounts of tars. At 850 °C, D11-10 gave much more naphthalene than D11-11, for the layered combination, besides markedly more toluene and benzene. These differences persisted at 900 °C.

The catalyst used previously has less contaminants than D11-10. The production of D11-11 was, however, discontinued and according to the supplier D11-10 was intended to replace the previous silica.

Table 13 Naphthalene and total chromatographable light aromatics heavier than benzene (in mg/g dry raw material) after tar decomposition of pyrolysis gas from birch or *Miscanthus* over dolomite, silica (D11-11) and combinations of these two catalysts at 850 and 900 °C

| Compound | Birch | | | | *Miscanthus* | | | |
| | 850 °C | | 900 °C | | 850 °C | | 900 °C | |
	Naphtha-lene	Total light aromatics excl benzene	Naphtha-lene	Total light aromatics excl benzene	Naphtha-lene	Total light aromatics excl benzene	Naphtha-lene	Total light aromatics excl benzene
30 g dolomite	2.4	7.1	1.6	4.4	2.6	7.5	3.4	6.8
30 g SiO$_2$	2.4	8.2	1.9	5.4	3.2	12.3	3.4	6.3
30 g SiO$_2$ + 30 g dolomite, mixed	2.0	6.5	0.6	1.6	2.7	7.4	2.8	5.2
47 g SiO$_2$ + 30 g dolomite, mixed	1.8	5.2	0.5	1.5	3.5	8.9	2.3**	3.8
60 g dolomite	1.5	4.1	0.2	1.0	3.7	10.1	2.3**	4.5
30 g SiO$_2$ + 30 g dolomite, layered	0.9*	2.4*	0.1*	0.5*	1.8	5.4	1.3	2.4

* Temperature in the cracker was 20-25 °C too high during the experiment

** Value increases over time during the experiment

Table 14 shows benzene and all light tar components analysed for the runs with only 30 g dolomite and only 30 g D11-11 at 850 and 900 °C, respectively. The results for the runs at 850 °C show that there is more benzene after decomposition over only silica than after tar decomposition over dolomite. Otherwise the results for the two catalysts are similar. At 900 °C, 30 g D11-11 gives somewhat more naphthalene from birch than 30 g dolomite does. The results obtained for the two catalysts separately do not indicate why the layered combination, using D11-11, has better effect.

For *Miscanthus* (see Table 13), more naphthalene and total light aromatics are produced with 60 g dolomite than with 30 g dolomite at 850 °C. This could be seen as unexpected, but may be explained by a greater portion of heavy tar being cracked to lighter tar, available for SPA analysis, when the larger amount of dolomite is used. Otherwise tar from *Miscanthus* follows the same trends as birch tar. Also for *Miscanthu*s the best results were obtained using 30 g silica (D11-11) and 30 g dolomite in separate layers.

Table 14 Individual light tar compounds and benzene (in mg/g dry raw material) after tar decomposition of pyrolysis gas from birch at 850 and 900 °C over dolomite or silica

Catalyst	850 °C		900 °C	
	30 g dolomite	30 g SiO$_2$ (D11-11)	30 g dolomite	30 g SiO$_2$ (D11-11)
Benzene	2.8	6.3	7.3	7.0
Toluene	2.1	2.6	1.3	1.5
m-/p-Xylene	0.4	0.5	0.2	0.3
o-Xylene	0.4	0.6	0.1	0.2
Indene	0.1	0.2	0	0.1
Naphthalene	2.4	2.4	1.6	1.9
2-Methylnaphthalene	0.3	0.3	0.1	0.2
1-Methylnaphthalene	0.1	0.2	0	0
Biphenyl	0.3	0.2	0.2	0.1
Acenaphthylene	0.1	0.3	0.1	0.1
Fluorene	0	0.1	0	0.1
Phenanthrene	0.4	0.4	0.3	0.3
Anthracene	0.1	0.1	0.1	0.1
Fluoranthene	0.2	0.1	0.1	0.4
Pyrene	0.2	0.1	0.1	0.1
Total light aromatics excluding benzene	7.1	8.2	4.4	5.4

The rice husk gasification in India was conducted using a natural material. For natural materials, also dolomite, even minor variations in composition may have great importance.

8 HETEROGENEOUS ALKENE OLIGOMERIZATION (V)

The acid-catalysed oligomerization of propene and butene was introduced in 1930, the first commercial catalytic process of the petroleum industry. The product was gasoline-range iso-olefins (C_6-C_{10}) using phosphoric acid impregnated on silica clay. Ethylene and propene were instead best oligomerized in the presence of phosphoric acid; kieselguhr with 60 % P_2O_5 became an item of commerce. Because of corrosion problems other acidic solid catalysts like zeolites were then studied to replace the phosphoric acid-containing catalysts. The shape-selective zeolites have also been investigated as catalysts for improving liquid product selectivities in oligomerization of low molecular weight olefins into liquid products.

At present ZSM-5 is known to be the most promising catalyst for the conversion of light olefins to higher molecular weight distillate fuels and/or gasoline, and is by far the most utilized zeolite since it is employed in the MOGD process.

The review focuses on oligomerization in heterogeneous systems. It provides a survey and a supplement to earlier reviews of alkene oligomerization by solid catalysts. Related publications and patents up to mid-1998 have been reviewed and evaluated in terms of catalytic systems used, reaction conditions and product selectivity.

Oligomerization of low molecular-weight alkenes leads to the formation of liquid fuel and synthetic lube oils, whereas the oligomerization particularly of high molecular-weight alkenes results in different synthetic lube oils. The unsaturated oligomer products are then hydrogenated to improve their oxidative stability, or alternatively, are used as feedstocks for various chemical processes using heavy olefins.

Oligomerization occurs in the presence of catalysts, and consists of two steps, propagation (chain growth), and elimination (hydrogen elimination from a β carbon to the catalytic centre); k_p and k_e denote the rate constants for the propagation and elimination reactions, respectively. If $k_p \gg k_e$, polyolefin will be formed, when $k_p \ll k_e$, dimers are obtained, and finally when $k_p \approx k_e$ oligomers are produced.

The oligomerization reactions are not elementary and are often accompanied by various parallel reactions. As shown in Figure 12, there are several distinct reactions occurring. First, two olefins $C_x^=$, and $C_y^=$, will oligomerize to a single higher olefin $C_{x+y}^=$ where x and y refer to olefin carbon numbers. Starting with a propene feed, for example, this reaction would yield the oligomers $C_6^=$, $C_9^=$, $C_{12}^=$ *etc.* Depending on catalyst nature, double-bond and skeletal isomerization have been reported. Additionally, any two olefins may react to disproportionate, via a carbenium ion intermediate, to two olefins of different carbon numbers. Olefin cracking may also occur simultaneously with oligomerization and disproportionation. Hydrogen transfer, cyclization, and aromatization may also take place.

Several mechanistic manners for the oligomerization of olefinic feedstocks have been suggested:

1. the carbenium ion species intermediate
2. surface ethoxy structure intermediate
3. cationic intermediate
4. cyclic derivatives intermediate
5. an ionic mechanism

The proposed mechanisms 1-3, which can describe the oligomerization of olefins over zeolites, such as ZSM-5, Y, *etc.*, are also called hydride intermediate mechanisms. Simplified schemes for the adsorption site for these three suggested mechanisms could be illustrated as in Figure 13. Spectroscopic results of olefin oligomerization over HZSM-5, which contained Brønsted acid sites showed that the product was linear oligomers and a mechanism similar to the one shown in Figure 13-a was proposed, though the mechanism has also been suggested to produce branched C_2-C_7 oligomers. The mechanism in Figure 13-b has also been proposed to give linear oligomers over high-silica zeolites possessing strong Brønsted acid sites.

Infrared spectroscopic data have shown that cationic oligomerization (Fig. 13-c) was initiated by Lewis acid sites of a dehydroxylated zeolite. The obtained products were mainly branched oligomers.

It has been reported that oligomer-chain branching depends on the zeolite porosity, and that long-chain olefins in good yields were obtained using zeolites with large

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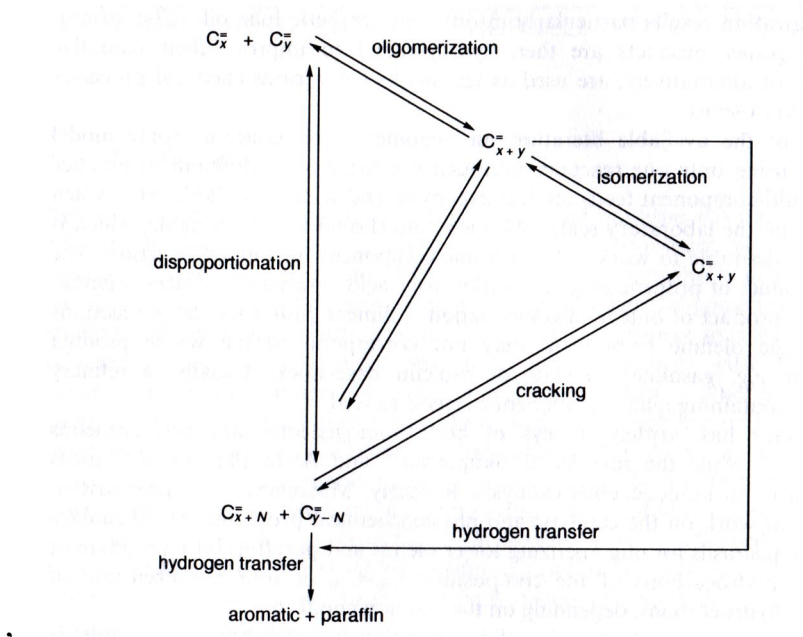
Figure 12 Olefin oligomerization reaction scheme

pore size while experimentally, it was found that the degree of chain branching decreases with pore size, *i.e.* omega > HY > mordenite > ZSM-5 > offretite > boralite for propene oligomerization.

The fourth mechanism, losing methyl branches through a protonated cyclopropyl intermediate, was suggested for obtaining linear products from dec-1-ene and isobutene. However, linear products were obtained over modified zeolites and branched products over unmodified zeolites. This would seem to imply that it is the channel in the zeolite rather than a cyclic intermediate which governs product structure. However, this mechanism has also been assumed to be the intermediate in order to explain the primary product distribution in oligomerization reactions over NiO on silica-alumina catalysts.

The ionic mechanism was used to explain the activity and selectivity behaviour in the oligomerization of olefins over alkali metal ion-exchanged zeolites. The activity pattern for the alkali metal ion forms in zeolites, in olefin oligomerization, is inversely proportional to the ionic radius, *e.g.* $Li^+ > Na^+ > K^+ > Rb^+$, thus, the carbenium mechanism does not explain this behaviour. For an ionic mechanism, the spatial constraints within the zeolite determine the selectivity routes towards the oligomerization reaction. According to this approach, the entry of further olefin molecules, which would lead to polymerization is impeded.

8.1 Ethylene oligomerization

The most important product in ethylene oligomerisation is α-olefins. Current commercial processes for making α-olefins are based on homogeneous catalysts. The product spectrum for heterogeneously oligomerized ethylene is more diversified than for homogeneously oligomerized ethylene, products tend to include
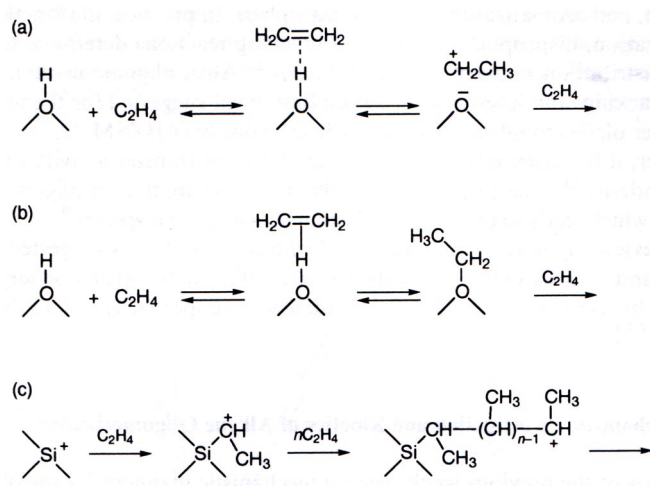
Figure 13 Adsorption mechanisms mechanisms; (a) carbenium ion mechanism (adsorption on Brønsted acid sites), (b) ethoxy structure mechanism (adsorption on Brønsted acid sites), (c) cationic mechanism (adsorption on Lewis acid sites)

both paraffins and aromatics. Since ethylene has a relatively low reactivity in comparison with other light hydrocarbons, methods have been developed to counteract the low reactivity, especially when the feed consists of a mixture of C_2-C_5 hydrocarbons.

8.1.1 Zeolites

It is reported that with zeolites having an internal/external surface area ratio of greater than 300 the contribution of external active sites to reaction can be assumed to be negligible, whereas for small zeolite crystallites, less than 100 nm in diameter, the effects of the external activity can become important, particularly for very rapid reactions or highly diffusion-limited reactions. ZSM-5, synthesized to give small size crystals, was used in the oligomerization of ethylene. The catalytic lifetime was related to the relative rate of the coke formation on the external and internal surfaces of the small crystal-size zeolite. Coke formation was less favoured on the external surface area in comparison to the internal one. It was concluded that the largest external surface area results in the longest lifetime. The shape selectivity was diminished with large external surface area and more C_{9+} aromatic hydrocarbons were formed.

8.1.2 Other solid-acid catalysts

The most investigated Ni-catalysts in oligomerization of ethylene deal with homogeneous systems. The majority of the investigated heterogeneous Ni-catalyst systems have deactivated rapidly and have been incapable of achieving steady-state reaction performances.

8.2 Propene oligomerization

Gasoline (C_5-C_{10}) is readily formed at elevated temperature and moderate total pressure, from ambient to about 5.5 MPa. At moderate temperature and relatively high pressure, the conversion conditions favour $C_{20}+$ aliphatic products, with a boiling point of at least 165 °C.

Trimers are the main product of propene oligomerization, while ethylene mainly forms dimers.

8.2.1 Zeolites

Since the HZSM-5 zeolite has a strong activity for hydrogen transfer, olefins in the reactants are partially hydrogenated to the corresponding paraffins by the hydrogen released during simultaneous aromatization, giving a decrease in selectivity to gasoline range hydrocarbons. However, the medium-pore, shape-selective HZSM-5 zeolite used in oligomerization of propene produced oligomers with a significantly less complex structure compared to those from conventional acid catalysts.

It is believed that two modes of olefin oligomerization can take place over shape-selective acidic zeolites, such as HZSM-5. One reaction sequence takes place at Brønsted acid sites inside the channels, producing essentially linear materials. The other reaction sequence occurs on the outer surface, producing more branched material. By decreasing the external surface acidity of such zeolites, reduced methyl-branching occurs, resulting in products of higher viscosity index and higher cetane number. On the other hand, it has been found that low-temperature oligomerization takes place on the outer surface of HZSM-5 crystals, whereas the high temperature formation of aromatics takes place inside the zeolite channel.

8.2.2 Other solid-acid catalysts

$NiSO_4$ / γ-Al_2O_3 catalyst was used in oligomerization of C_2-C_4 alkenes. It was presumed that two different characteristic active sites in the $NiSO_4$ / γ-Al_2O_3 catalyst accounted for the olefinic reactions. The coordination sites contributed to dimerization of ethylene, while oligomerization of propene proceeded both via coordination and acidic sites. However, 1-butene only oligomerized via acidic sites.

When, in another study, nickel was incorporated onto silica-alumina by various methods it was found that homogeneous precipitation was most active in propene oligomerization.

Also catalysts containing nickel supported by or incorporated into clay structures have been used for oligomerization. It has been shown that nickel-substituted micamontmorillonite is a very active catalyst for oligomerizing propene and butene.

8.3 Butene oligomerization

Lower olefins are produced in large quantities by cracking processes like steam or fluid catalytic cracking. For many years, the usage of the C_4-olefins has been limited to mainly alkylate production, gasoline blending or simply burning.

The elimination of lead in gasoline initiated the development of methyl-tert-butylether (MTBE) production from isobutene and methanol. Nowadays, MTBE is an integral component of the gasoline pool, and still rapidly increasing demand will result in a more or less quantitative consumption of the isobutene contained in C_4-cuts. Further, sometimes there is insufficient isobutene available in a refinery to permit all olefins from the different cuts to be catalytically alkylated to MTBE.

8.4 Long-chain alkene oligomerization

The light olefinic feedstocks alone or in admixture with paraffins are converted into liquid fuels by contacting the feedstocks with a catalyst containing an acidic solid. Light olefins can also be oligomerized to α-olefins (RCH=CH, where R is an alkyl radical of 8 to 22 carbon atoms) or internal olefins (R´CH=CHR´´, where R´ and R´´ are the same or different alkyl radicals of 1 to 21 carbon atoms). Synthetic

lubricants are produced by the oligomerization of alpha or internal, linear or branched alkenes or 1-alkenes.

There are still efforts to improve the performance of natural mineral oil-based lubricants by the synthesis of oligomeric hydrocarbons, which has been the subject of important research and development in the petroleum industry for many years and has led to commercialization of a number of synthetic lubricants. These materials are based on oligomerization of α-olefins such as C_6-C_{20} olefins. Industrial research effort on synthetic lubricants has generally focused on improved viscosity index, thermal and oxidative stability, and a pour point equal to or better than that of the corresponding mineral oil lubricants.

It is common practice to classify the base stocks by their viscosities, measured in centistokes (cSt) at 100 °C. The low viscosity materials, less than or equal to about 4cSt, are recommended for low temperature applications. Motor oil, turbine lubricants and other industrial lubricants generally require medium viscosity base stocks, *i.e.* 4-8 cSt. High viscosity base stocks, 40–100 cSt, are used in gear oils and as blending stocks.

The degree of oligomerization is affected by the catalyst and reaction conditions, as well as the length of the carbon chain of the monomer used as starting material. Fluids prepared from short chain monomers have low pour points and low viscosity indices, whereas fluids prepared from long chain monomers have moderately low pour points and higher viscosity indices. Oligomers prepared from long-chain monomers are generally more suitable than those prepared from shorter-chain monomers for use as medium viscosity synthetic lubricants.

8.4.1 Zeolites

Synthetic lubricant with improved viscosity index was prepared by oligomerization of the C_{10}-C_{20} 1-alkenes over catalysts containing large pore zeolites with high silica to alumina ratio. It was found that the reactivity of alpha-olefins followed the order of dodecene > tetradecene > hexadecene. In general, internal alkenes are less reactive than the corresponding α-alkenes and conversion in oligomerization decreases as the chain lengths of the feed alkenes increase.

8.5 Dimerization of alkenes

It is well known that olefins dimerize on contact with a nickel oxide catalyst at elevated temperature. Since the discovery of their specific activity in catalyzing dimerization reactions, nickel-based catalysts have been the subject of intensive mechanistic and kinetic studies directed toward identifying and understanding the active sites responsible for this property. Earlier nickel catalysts were homogeneous, however, nickel deposited on different supports has shown high selectivity towards alkene dimerization.

The main product from ethylene dimerization is 1-butene which is useful as a co-monomer in polyethylene production. Usually, the homogeneous titanium catalytic system is established in the commercial production routes.

The conventional processes used in the dimerization of isobutene are generally based on the use of an acidic catalyst, such as sulfuric acid or polyphosporic acid (in liquid or supported by an inorganic solid). The conversion of C_3 or C_4 olefins into dimers using catalysts consisting of nickel deposited on silica or silica/alumina and zeolite supports is also recognized. The obtainable dimers from oligomerization of propene and butene, such as hexenes and octenes are particularly useful for conversion by the well-known oxo alcohol process into the corresponding heptyl and nonyl alcohols which may be used in the production of plasticizers, lubricating oil additives, detergents, defoamers, and similar products. Dimers of propene are used to improve octane rating in gasoline.

In general, however, the solid catalysts reported so far are not as good as the currently used commercial systems, especially the homogeneous nickel-based catalytic systems.

8.6 Enterprises mainly involved

The patents on heterogeneous oligomerization quoted in the review were mainly conceded to major oil and oil processing companies. More than 75 %, *i.e.* 91 of a total of 121 patents, came from eight enterprises which each has four or more patents. This can be seen in Figure 14. Of the eight enterprises, four produce α-olefins homogeneously from ethylene.

In 1966 Gulf (acquired by Chevron in 1983) became the first manufacturer of commercial high-purity α-olefins from ethylene oligomerization [109]. The process uses a homogeneous catalyst (triethylaluminium), even carbon-number α-olefins in the range C_{10}-C_{20} are produced.

Chevron's patents concerning heterogeneous catalysis date from the 80's and mostly concern the production of liquid fuels from propene using ZSM-5 [110-112] or silicate molecular sieves [113, 114]. A patent for production of lube oil from higher olefins using ZSM-5 and crystalline metal silicate was also conceded [115].

Shell produces α-olefins from ethylene since 1977. SHOP (Shell Higher Olefin Process) is a three-stage process utilizing a homogeneous nickel catalyst in the first oligomerization stage. The use of three stages allows tailoring carbon number distribution and amount of desired α-olefin, usually C_{10}-C_{20} [109].
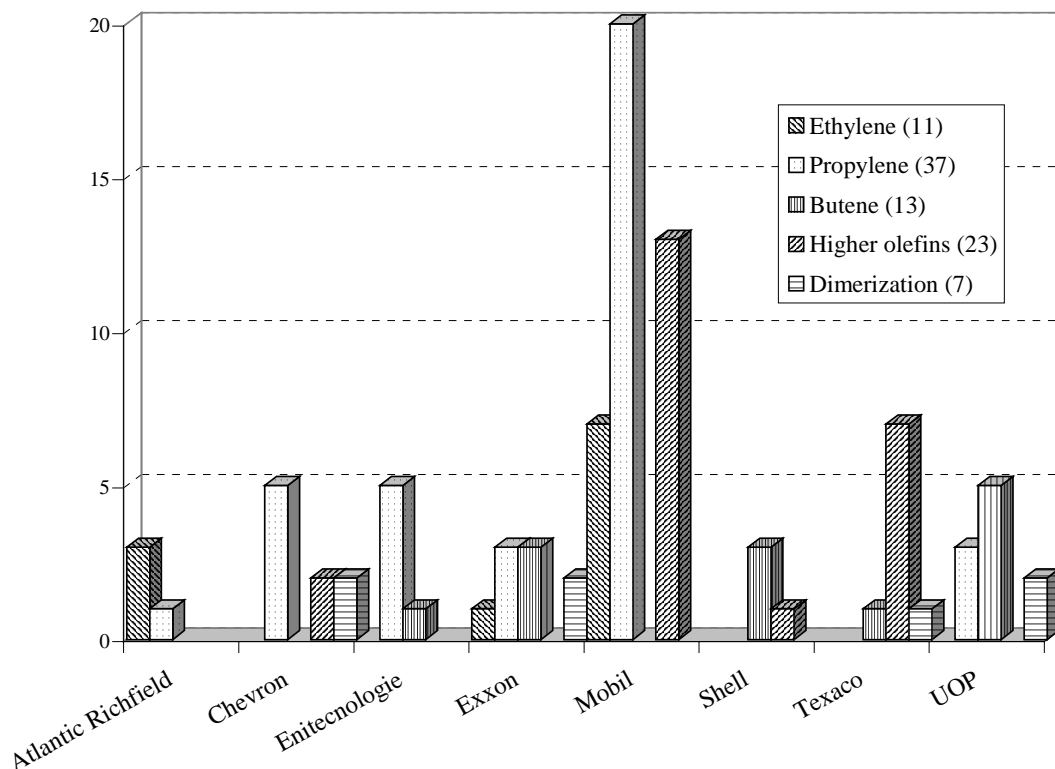
Figure 14 Enterprises mainly involved in heterogeneous oligomerization and number of patents conceded 1971-1997

The patents issued to Shell on heterogeneous oligomerization, the last one dating from 1991, mainly concern oligomerization of butene using nickel or mordenite to produce liquid hydrocarbons [116, 117]. Also a method for producing synthetic lubricant from higher olefins using $TaCl_5$-SiO_2 was patented [118].

UOP has recently developed the Linear-1 process for linear α-olefin production from ethylene using a proprietary homogeneous catalyst [119]. According to UOP, the process offers flexibility in varying the C_4-C_{10} yield from 40 to 75 % by making simple adjustments to the operating parameters.

UOP's most recent patent on heterogeneous oligomerization dates from 1989 and concerns oligomerization of butene using alumina impregnated with $Ni(NO)_3\cdot6H_2O$ and $SnCl_4\cdot5H_2O$, then activated with $AlCl_3$ and Et_2AlCl [120].

Exxon has developed a process where ethylene is oligomerized to very pure linear α-olefins with a soluble alkylammonium chloride/titanium tetrachloride catalyst at temperatures between –70 and +70 °C in organic solvents. The molecular weights of the olefins increase with increasing reaction temperature and decreasing polarity of the solvent [121].

Exxon has also been been active in heterogeneous propene oligomerization in the 90's. In 1996 a patent was obtained for using a molecular sieve ion-exchanged with

ammonium chloride, ammonium nitrate or ammonium hydroxide to produce an olefinic oligomer, the less branched oligomers usable in alkylation of aromatic hydrocarbons in the manufacture of surfactants and polyolefin stabilizers [122]. The year before, a patent was obtained for using various combinations of ZSM-22 and ZSM-5 [123]. The products contain less C_6 and more C_{15+}, the greater the share of ZSM-5, conversion around 90 % for all cases. In 1993 a patent was obtained for using ammonium chloride-exchanged ZSM-22, where conversion was found to increase with increasing water content of the feed [124].

During the 90's Exxon also obtained a patent on oligomerization of butene using a catalyst with a monolayer of SiO_2 on Al_2O_3. Products are claimed to be C_8, C_{12} and C_{16} olefins with selectivities of 59.7, 17.3 and 6.7 %, respectively [125]. Exxon's most recent patent on dimerization, dating from 1995, also concerns butene. The catalyst contains 50 % NiO, 13 % TiO_2 and the remainder is either SiO_2 or 27 % SiO_2 and 10 % Al_2O_3. The first catalyst gives 53% butene conversion and the product is 73 % C_8-oligomers of which n-octane is 24 %. The second gives 78 % butene conversion with 62 % C_8-oligomers of which n-octane is 21 % [126]. Exxon and Mobil merged in 1999, but this was after the patents discussed in the review.

BP Amoco does not have any recent patents on heterogeneous oligomerization, but it still has homogeneous production of α-olefins. The process was originally developed and owned by Ethyl Corporation [127].

The remaining four enterprises with substantial research on heterogeneous oligomerization have had various interests and methods of appproach. Atlantic Richfield obtained three patents in the 80's on oligomerization of ethylene using ZSM-5 and modified ZSM-5 to produce C_{5+} [128-130].

Enitecnologie has been active in propene oligomerization in the 90's with two patents employing silica-alumina gel [131, 132]. The latest, from 1995, is for the production of gasoline and jet fuel. The patent from 1993 concerns either propylene or butene oligomerizationon over SiO_2/Al_2O_3 with a small amount of NiO added, with conversions of 79 and 44 %, respectively.

Texaco's interest during the 90's has focused on oligomerization of higher olefins, with seven patents. The products obtained are mainly suitable as synthetic lubricant base stock. The catalysts in the earlier patents are based on montmorillonite clay [133-136] while the later are based on sulfate-activated TiO_2 or ZrO_2 [137-139], in one case physically blended with an acidic montmorillonite.

Mobil is in a special category as to the number of patents obtained on heterogeneous oligomerization. During the 90's five patents concerning only ethylene have been procured. Not surprisingly, the catalysts used are varieties of ZSM-5 [140-142] and, in the later patents, surface-deactivated ZSM-23 or ZSM-5 [143, 144]. The products are C_{5+} gasoline, dewaxed distillate, substantially linear oligomers suitable as alkylating agents as well as lubricating oil or high cetane additives (after hydrogenation).

Also five patents on propene oligomerization were obtained during the past decade. The most recent patent in the review utilizes WO_3 supported on ZrO_2 by either impregnation or co-precipitation [145]. The co-precipitated catalyst gave 29.5 % gasoline, 61.6 % diesel and 8.9 % lube oil; the corresponding figures for the impregnated catalyst were 38.5, 56 and 5.5 %, respectively.

Seven patents on oligomerization of higher olefins were obtained by Mobil during the 90's. Several types of catalysts have been used: halide on SiO_2 [146], various forms of Cr [147-150], MCM-41 with [151] or without [152] group VIB metal impregnation (preferably Cr). The products are mostly suitable as lubricants.

8.7 Conclusions

Many advantages can be gained if a homogeneous catalyst can be supported on a solid phase without any significant loss in activity. But usually there is insufficient ability in these catalytic systems to control the extent of oligomerization, and there is also a lack of selectivity to the formation of desired products. A problem which is common to many conventional oligomerization catalysts lies in the corrosive action of the acids used.

In practice, the feedstock for oligomerization of low and/or high molecular weight olefins is usually some refinery cut, constituting a multicomponent system. More work in this area, multicomponent feedstocks and solid catalysts, is needed.

Progress in the development of adequate equipment design for solid catalytic oligomerization, *e.g.* reactive distillation, is also needed. Since a solid catalytic system often implies frequent catalyst deactivation, it seems reasonable that the development of the catalytic system should be accompanied by a more convenient process and improved upgrading of oligomerization products.

9 CONCLUSIONS

Peat and wood are considerably more easy to liquefy than coal in a hydrogen-donating solvent. The higher the initial hydrogen content of the solid fuel, the longer is the initial conversion period in which no hydrogen consumption from the hydrogen-donating solvent occurs.

For peat dissolution in a simulated recycle solvent, it was found that the amount of solid residue depends on the amount of tetralin (hydrogen donor) and on the total amount of aromatic carbon present in the solvent. Increased aromaticity of liquefaction solvent increases dissolution at a given concentration of hydrogen donor. To achieve effective use of potentially available hydrogen for peat dissolution, the solvent must have enough physical dissolving ability, *i.e.* aromaticity. It is doubtful whether the maximum degree of dissolution achieved in the experimental series reported in Paper III is large enough for a process for peat liquefaction. Though the amount of solid residue is only 14 %, it contains slightly above 20 % of the energy in the dried raw material. This is probably in excess of what is needed for the production of energy and gas required for a process.

The amount of donatable hydrogen may probably not be increased by further hydrogenation of the process-derived solvent if it contains only 44 % aromatic carbon. However, analysis of the high-boiling fractions of the experiments achieving the highest dissolution indicates that that aromaticity of dissolved product increases with degree of dissolution. This may represent a possibility for obtaining a peat-derived recycle solvent with a higher percentage of donatable hydrogen. Especially for peats of high heating value parameters more closely resembling those for coal liquefaction must be used to obtain a satisfactory dissolution.

Tar from biomass gasification may be cracked using dolomite, when sufficient temperature and residence time are applied almost only benzene and naphthalene remain after cracking. Benzene is not a problem, it contributes to the heating value of the product gas, but naphthalene causes problems in downstream equipment. The use of a combined catalyst consisting of a layer of silica above a layer of dolomite, *i.e.* the gas passes the silica first, decreases naphthalene concentration considerably. Even small concentrations of contaminants in the silica, however, influence the results.

Many advantages can be gained if a homogeneous catalyst can be supported on a solid phase without any significant loss in activity. But usually there is insufficient ability in these catalytic systems to control the extent of oligomerization, and there is also a lack of selectivity to the formation of desired products.

In practice, the feedstock for oligomerization of low and/or high molecular weight alkenes is usually some refinery cut, constituting a multicomponent system. More work in this area, multicomponent feedstocks and solid catalysts, is needed.

Progress in the development of adequate equipment design for solid catalytic oligomerization is also needed. Since a solid catalytic system often implies frequent catalyst deactivation, it seems reasonable that the development of the catalytic system should be accompanied by a more convenient process and improved upgrading of oligomerization products.

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68

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