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Citation for the published paper:
Hansson, K. ; Samuelsson, J. ; Åmand, L. et al. (2003) "The temperature's inuence on the selectivity between HNCO and HCN from pyrolysis of 2,5-diketopiperazine and 2-pyridone". Fuel, vol. 82 pp. 2163-2172.

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The temperature's influence on the selectivity between HNCO and HCN from pyrolysis of 2,5-diketopiperazine and 2-pyridone☆

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Received 2 May 2003; revised 5 June 2003; accepted 10 June 2003; available online 24 June 2003

Abstract

Two cyclic amides, 2-pyridone and 2,5-diketopiperazine (DKP), were pyrolysed at temperatures ranging from 700 to 1100 °C. Pyridone is the only one of the four main nitrogen functionalities found in coal that is likely to form HNCO under pyrolysis. DKP is a primary pyrolysis product from proteins, which are the main nitrogen source in biomass. The formation of HNCO from biomass has been suggested to originate from DKP and other cyclic amides. The aromatic 2-pyridone was thermally more stable than the non-aromatic DKP. Both amides formed HCN, HNCO and NH_3. The NH_3 yields, about 3–4% for 2-pyridone and 10% for DKP, were almost independent of temperature. The HCN yield on the other hand showed strong temperature dependence and increased with temperature for both of the cyclic amides. The HNCO yield decreased with increasing temperature for DKP over the whole temperature interval. For 2-pyridone, the pyrolysis was incomplete at the lowest temperature in the investigation. Between 900 and 1100 °C, the pyrolysis of 2-pyridone was complete and the HNCO yield decreased with increasing temperature. The HNCO/HCN ratio for both of the cyclic amides decreased with increasing temperature over the whole investigated temperature range. The finding in literature that the HNCO formation from cracking of coal tars produced a maximum HNCO yield at an intermediate temperature, is explained by the thermal stability of pyridone at low temperatures and the selectivity towards HCN at high temperatures.
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Keywords: Pyrolysis; Biomass; Coal; Pyridone; Diketopiperazine; HNCO

1. Introduction

The release of fuel nitrogen during pyrolysis of coal is greatly affected by the rank of the coal [1]. The exact chemical structure of coal is usually unknown, but the chemical functionalities are better known. XPS investigations of coal have revealed that the nitrogen functionalities in coal give rise mainly to three different nitrogen 1s binding energies, 398.7, 400.3 and 401.4 eV [1–4]. The peak at 398.7 eV is typical for pyridinic nitrogen, whereas the peak at 400.3 eV is typical for pyrrolic nitrogen, but also for amide nitrogen [5] and in particular for pyridone [3]. The peak at 401.4 eV is usually referred to as quaternary nitrogen [1–4], but the nature of this nitrogen functionality is still poorly understood. It has been suggested that the quaternary peak could correspond to oxidated pyridinic nitrogen [4], since oxidative surface preparation was found to increase the intensity of the 401.4 eV peak on behalf of the intensity of the pyridinic peak. Amines have also been mentioned as possible sources to the quaternary peak [1]. In fact, amino acids and a variety of amines in their protonated state have N 1s binding energies of about 401.4 eV [6]. X-ray absorption near-edge spectroscopy (XANES) has indicated the presence of four nitrogen functionalities in coals [7]. As from most XPS studies, pyrrolic and pyridinic nitrogen functionalities were found. Furthermore, aromatic amines and pyridone functionalities were suggested. It is not possible by means of XPS to distinguish between quaternary nitrogen and amine nitrogen or between pyrrolic nitrogen, amide nitrogen [5] and pyridone nitrogen [3]. XPS measurements on coal and methylated coal revealed that some of the 400.3 eV signal from the parent coal disappeared after methylation, which indicates that some of the nitrogen that gives rise to the 400.3 eV peak for the coal was something other than

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doi:10.1016/S0016-2361(03)00206-0

pyrrolic nitrogen. It was suggested that the methylated nitrogen was pyridone nitrogen [3]. That pyrrole, pyridine and pyridone functionalities are present in coal is clear. Whether or not amines are also present in coals is not undisputed in literature.

Different nitrogen functionalities are expected to have different pyrolysis characteristics and to give different pyrolysis products. A clear correlation between quaternary nitrogen (from XPS measurements) and formation of NH_3 has been found [1]. This correlation supports the idea that what is called quaternary nitrogen in fact is aromatic amines. The pyrolysis of pyrrole and pyridine has been the subject of several studies. Pyrolysis of pyrrole produced alkyl-cyanides and hydrogen cyanide exclusively [8,9]. Pyrrole is thermally stable due to its aromatic structure, and high temperatures or long reaction times are necessary to get high degrees of conversion (Fig. 1). For pyridine, the product yields were found to depend on the reactor wall material. In nickel and stainless steel reactors, pyridine formed mainly N_2 under experimental conditions, whereas a quartz reactor preferentially formed HCN [10]. Pyridine not only decompose through pyrolysis reactions, but also through bimolecular reactions is the reason why the decomposition rate increases with pyridine concentration [10,11]. Nitrogen containing pyrolysis products from pyridine include HCN and nitriles [10–13]. Aromatic nitrogen species have also been found [10,13]. In some experimental studies, especially in those employing high pyridine concentrations, a carbonaceous residue was formed [10,11]. This residue was found to catalyse pyridine decomposition [10]. NH_3 has also been found from pyridine decomposition [10,14]. In a compilation of literature data on pyrolysis of pyrrolic and pyridinic model compounds [15], it was stated that; "the formation of NH_3 during pyrolysis appears to be related to the formation of "high molecular mass materials", "tarry materials" or soot". The proposed

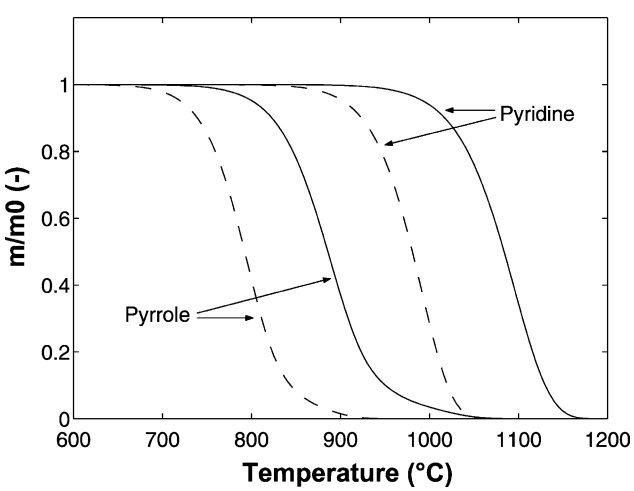

Fig. 1. Pyrolysis of pyrrole and pyridine at residence times of 0.5 s (solid lines) and 10 s (dashed lines) predicted by kinetic data from literature [8,12].

relation between formation of NH_3 and high molecular residuals may contribute to the overall conversion of pyridine, but the difference in product yields and rates of pyridine pyrolysis found in literature, is here believed to be an effect of catalytic surfaces. In the study where the highest NH_3 yields were found [14], the temperatures were so low that the pyridine conversion would be expected to be close to zero from the pyrolysis rates calculated from kinetics derived from other studies on pyridine pyrolysis [10,12,13]. Furthermore, the degree of conversion was almost independent on reactor temperature and gas residence time. It was postulated that a large portion of the pyridine decomposed in the heated gas line [14], and under oxygen free conditions, virtually all decomposition of pyridine occurred in the heated gas line. This decomposition was probably the result of catalysis rather than pyrolysis. In one out of two studies, where about 50% of the decomposed pyridine was converted into a solid residual, a minor portion of the volatile nitrogen was identified as NH_3 [10] while NH_3 was not observed at all in the other study [11]. This implies that in the absence of catalytic surfaces, HCN and nitriles are the main pyrolysis products from pyrrole and pyridine.

Pyrolysis experiments with model coals, prepared from cellulose and either 2-hydroxycarbazole (pyrrolic nitrogen) or 6-hydroxyquinoline (pyridinic nitrogen) by compaction heat treatment [16], resulted in residual solid nitrogen, tar nitrogen (pyrrolic from pyrrolic coals and pyridinic from pyridinic coals) as well as HCN. However, it was found that calcium and iron in the sample decrease the yield of both char nitrogen and HCN nitrogen. Calcium catalysis also led to some NH_3 formation [16]. It was suggested that iron catalyses N_2 formation via solid-phase reactions. Similar trends have been observed in pyrolysis experiments with coal, demineralised coal, and demineralised coal with calcium added to it. Demineralised coal formed more HCN and less NH_3 than did the original coal and demineralised coal with calcium added. Demineralised coal also formed more char nitrogen and less N_2 than the original coal and demineralised coal after calcium addition [17]. Hence, not only the nitrogen functionality, but also the coal's mineral composition influences the nitrogen release from pyrolysing coal.

Apart from HCN and NH_3, HNCO has also been observed to be a pyrolysis product from coal [18]. Pyrolysis of coal tars, formed after pyrolysis of coal at 600 °C, also formed HNCO [19]. It was suggested that 2-pyridone or 2-pyrrolinone functionalities would be responsible for the formation of HNCO from coal [19]. As mentioned above, there are several results indicating that 2-pyridone is one of the most important nitrogen functionalities in coal. However, of the functional forms found in coal, most attention has been paid to the pyrolysis of pyrrole and pyridine. The pyrolysis of 2-pyridone will be investigated in this paper.

In previous work on pyrolysis of protein, it has been suggested that one of the main primary pyrolysis reactions is

the formation of 2,5-diketopiperazines (DKP) [20,21]. It was suggested that HCN and HNCO are primarily formed from secondary pyrolysis of DKP and other cyclic amides that might arise [21]. The formation of NH_3 was suggested to take place mainly in the solid phase [21]. Furthermore, it was suggested that the NH_3 forming reaction might dominate over HCN and HNCO formation for proteins with an amino acid composition that results in high char nitrogen yields. It was also suggested that cyclic amides of varying size would show similar temperature dependences on the selectivity between HCN and HNCO [20,21]. In order to gain more information on the mechanisms of protein pyrolysis, and to investigate the hypothesis that all cyclic amides have similar temperature dependences on the selectivity between HCN and HNCO, the pyrolysis of DKP was also investigated in this work.

2. Experimental

The DKP and 2-pyridone samples were purchased from Sigma Aldrich. Both samples consisted of fine powders. To avoid problems associated with introducing a powder into the reactor [20], the powders were compressed into tablets, which subsequently were crushed into fragments big enough not to be elutriated. The weight of the fragments ranged from 9 to 25 mg and they were all thinner than 0.5 mm. The particles were pyrolysed one at a time. Experiments with DKP were performed at 700, 800, 900, 1000 and 1100 °C. Experiments with 2-pyridone were made at 900, 1000 and 1100 °C. All of these experiments were made in triplicate runs. One experiment with 2-pyridone was also performed at 700 °C. At this temperature, most of the 2-pyridone was not pyrolysed and unreacted 2-pyridone condensed in the heated line downstream from the reactor. More than 1 h was needed to evaporate the condensed 2-pyridone from the lines so that new experiments could be conducted.

The fuels were pyrolysed in a fluidised bed reactor (Fig. 2). The reactor is a cylindrical quartz glass reactor with an inner diameter of 60 mm, placed in a vertical three-zone tube furnace that is electrically heated. The temperature is controlled separately in each zone. Gas is introduced into the bottom of the reactor and is heated in the first zone, 500 mm long. The quartz sand bed rests on a gas distribution plate that is located between the first and second zones. The second and third zones are 300 mm long, respectively. The bed material has sizes ranging between 250 and 315 μm and the static bed height was approximately 60 mm. The particles were fed from the top of the reactor through a small cylinder with two valves, one at the top and the other at the bottom. Through this cylinder, the particles could be introduced without letting air into the reactor and without causing too large changes of the gas flow pattern within the reactor, by always keeping one of the valves closed.

Experiments were made with nitrogen as fluidising gas. Reaction gases are withdrawn from the top of the reactor. Most of the gases leave the reactor as exhaust gas. However, pumps withdraw as much gas as the analysis instruments require. A filter placed on top of the reactor prevents bed material from entering the analysis system. After the filter, the gas stream is divided into three streams. One leads to a FTIR (Fourier Transform Infra-Red) instrument (Bomem

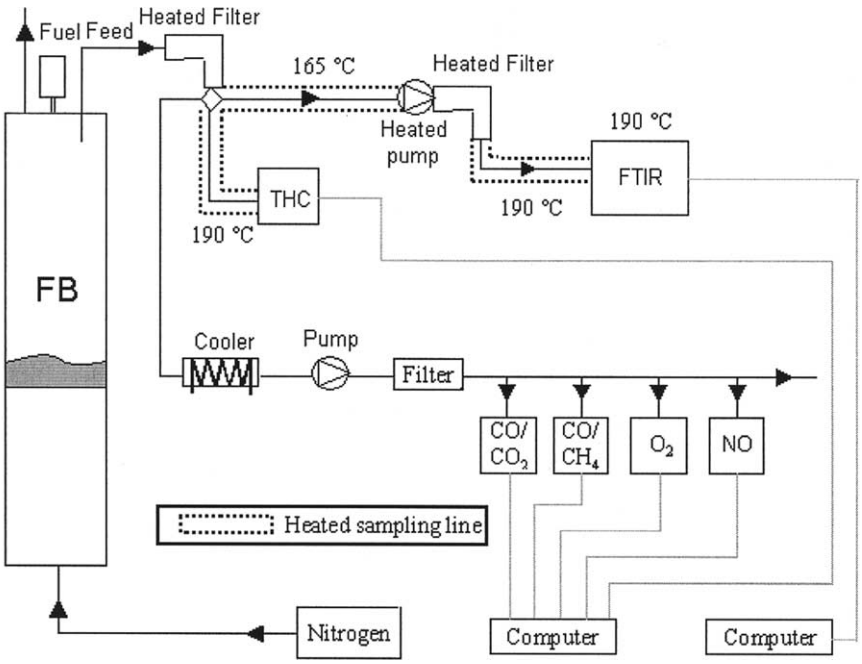

Fig. 2. The experimental set-up.

model 9100), one to a FID (Flame Ionisation Detector) instrument (J.U.M. Engineering model 3-300A), and one to two NDIR (Non-Dispersive Infra-Red photometer) instruments (Rosemount Binos 100), a paramagnetic O_2-analyser (Leybold-Heraeus AG, Oxynos-1) and a chemiluminescence NOx-analyser (ECO Physics). CO and CO_2 concentrations were measured with one of the NDIR instruments, total hydrocarbons were analysed with the FID. CH_4 was measured with the second NDIR instrument. HCN, NH_3 and HNCO were analysed with the FTIR. The data acquisition times were 1 s for all instruments except the FTIR, which had a data acquisition time of about 3 s.

Each of the peaks in the FTIR spectra from DKP was identified as belonging to one of the light gases NH_3, HCN, HNCO, CO, CO_2, CH_4, C_2H_4, C_2H_2 or H_2O. Trace amounts of other gases could also be present. For example, the NOx-analyser detected very low concentrations of NO (less than 0.01% of total nitrogen), which was not apparent from the FTIR spectra. Of gases not detectable by FTIR, only H_2 is expected to be formed in high yields. For 2-pyridone pyrolysed at 900–1100 °C, the spectra contained the same pyrolysis products as DKP, as well as some larger hydrocarbons. For 2-pyridone pyrolysed at 700 °C the FTIR spectra are dominated by structures that belong to tar products, 2-pyridone and possibly heavy pyrolysis products, as well as some of the gases observed at higher temperatures. Some of the gases observed at higher temperatures could not be observed at 700 °C, since the high absorbance of the tars in some regions of the IR spectrum made these regions unavailable for identification of other species.

The O_2-analyser was running continuously before, during and after each experiment and confirmed that no air entered the reactor. However, some oxidation of primary pyrolysis products might still take place, since the samples are hydrophilic and contain bonded water. The samples were not dried prior to pyrolysis, and consequently, rather high H_2O concentrations were observed during the experiments. In order to see if char was formed during the experiments, a stream of O_2 was led through the reactor after each experiment. No CO_2 was detected but the sensitive NOx-analyser showed NO concentrations of about 1–3 ppm in some of the experiments. This NO accounted for less than 0.02% of the total nitrogen, and so it was considered that the compounds were virtually completely volatilised. The nitrogen yields were calculated from the concentration curves under the assumption that all fuel-nitrogen was converted into HCN, HNCO, NH_3 and NO, and that the sum of the yields of these species were 100%. No yields were calculated from the experiment with 2-pyridone at 700 °C, since not all nitrogen species were accounted for in that experiment.

The concentrations of NH_3 and HCN were determined from the FTIR spectra, about 12 from each experiment, by spectral subtraction. No HNCO calibration spectra were available for the FTIR used in the experiments (FTIR1), but HNCO spectra from another FTIR (FTIR2), differing from the present FTIR only in gas cell volume and optical path length (l), were available. Ideally, the absorbance (A) at a specific wavenumber (ν) is linearly dependent on gas concentration (c), according to Bouguer–Lambert–Beers law ($A = alc$), where a is called the absorptivity. The absorptivity is gas specific and is a function of wavenumber. Ideally, $a(\nu)$ from the second FTIR instrument could be used to quantify HNCO in the spectra from the present experiments. $a(\nu)$ functions calculated from both FTIR instruments were compared for gases that absorb IR light in approximately the same spectral range as HNCO. In practice, the absorbance is often not linearly dependent on concentration. The non-linearity is mainly an effect of insufficient resolution. Many of the gases calibrated in the FTIR show linear absorbance-concentration correlations at low absorbance, but at higher absorbance the correlations deviate from the linear ones. Therefore, the $a(\nu)$ functions for the two instruments were calculated for comparable products lc. They were found to be identical for both CO and N_2O why it was assumed that the same should be true for HNCO as well. Hence, the HNCO spectra from FTIR2 were used in spectral subtraction. If the spectrum of HNCO with concentration c_2 from FTIR2 coincides with the unknown spectrum after spectral subtraction of CO and CO_2, then the true concentration (c_1) is calculated from Bouguer–Lambert–Beers law: $c_1 = c_2 l_{\mathrm{FTIR2}}/l_{\mathrm{FTIR1}}$. At the lowest temperatures, the HNCO concentrations were so high that in some spectra, all IR light of some wavenumbers around 2290 and 2240 cm^{-1} was absorbed by the HNCO. Consequently, the concentrations in these spectra could not be estimated by spectral subtraction. Instead, the absorbance at 2259.6 cm^{-1} was used for quantification. CO_2 also absorbs at this wavenumber, which was accounted for by subtracting the contribution of CO_2 from the absorbance at this peak. For FTIR2, the absorbance at this wavenumber was linearly dependent on concentration, and the absorptivity for the peak was calculated. This absorptivity was then used to estimate the high concentrations. Note that the absorbance at the highest concentrations was higher than for all of the concentrations for which FTIR2 was calibrated. Hence, it is possible that the linear correlation used here could give underestimates of the true concentrations.

For transient events, it is known that the analysed NH_3 concentrations are delayed in time, since ammonia adsorbs on the walls of gas sampling lines and other surfaces [22]. To avoid adsorption of ammonia in the gas line, the lines were heated. The temperature in the FTIR's gas cell is 190 °C, so to avoid that tars in the gas flow condenses in the gas cell, the first part of the gas line was heated only to 165 °C in order for the tars to condense there instead of in the gas cell. The filters and the pump located between the reactor and the FTIR were also heated to prevent ammonia adsorption. When all gas concentrations as

functions of time were normalised, all gas concentrations except for the concentration of NH_3 were found to coincide in time. For NH_3 the peak concentration was slightly delayed as compared to the other gases. It was therefore concluded that no other gas than NH_3 adsorbs to any significant extent in the gas line. Since the HNCO concentration curve had the same shape as all other concentration curves (except for NH_3), no non-linearity appears to make the HNCO concentration unreliable.

3. Results and discussion

The DKP was completely converted into gases even at the lowest temperature, 700 °C, used in this study. That was not the case for 2-pyridone, which was only partly pyrolysed at 700 °C. Both of the compounds used in the experiments are cyclic amides, 6 atoms in length. The 2-pyridone is more thermally stable than DKP, since the former is aromatic while the latter is not.

DKP forms HCN, HNCO and NH_3 at all temperatures studied. Trace amounts of NO were also found. The HNCO yield decreases and the HCN yield increases with increasing temperature, reaching an asymptotic value of 88% at 1000 °C. The NH_3 yield remains fairly constant at around 10% at all temperatures except 700 °C, where the yield is 15% (Fig. 3).

HCN and HNCO is formed from 2-pyridone. Small yields, about 3–4%, of NH_3 were also recorded at 900, 1000 and 1100 °C. At 700 °C, NH_3 could not be observed due to a strong absorbance of the tar in the region where NH_3 is usually found. Trace amounts of NO were observed for 2-pyridone as well. The HNCO yield decreases with increasing temperature (Fig. 4). The HCN yield increases with increasing temperature, reaching an asymptotic value of about 95% at 1000 °C.

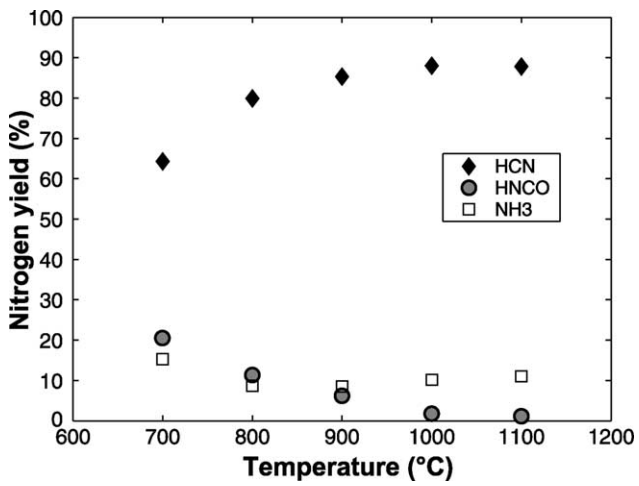

Fig. 3. Yields of HCN, HNCO and NH_3 for DKP as functions of temperature.

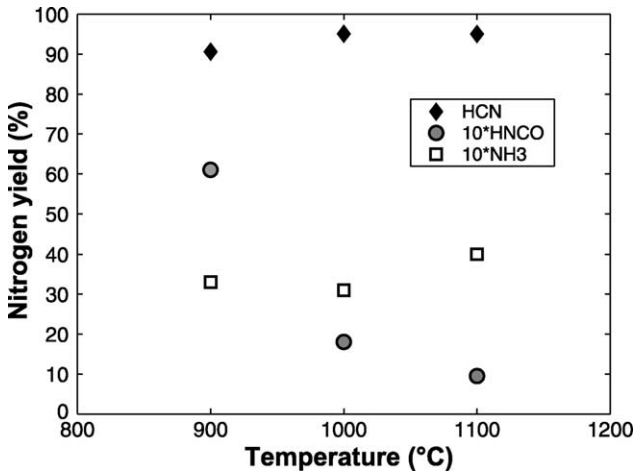

Fig. 4. Yields of HCN, HNCO and NH_3 for 2-pyridone as functions of temperature.

The 4-ring cyclic amide 2-azetidinone has been found to break down thermally via two competing reaction pathways [23] (Fig. 5). The only reaction observed at low temperatures was the one leading to HNCO and ethene. The other reaction that became important at higher temperatures was suggested to primarily form ketene and methylenimine. Although the latter product was not observed, ketene and HCN were observed, and it is well known that methylenimine is thermally unstable, readily decomposing to HCN and hydrogen gas.

From pyrolysis of DKP, HCN is a well-known product [24] and from pyrolysis of 3,6-disubstituted-2,5-diketopiperazines, nitriles are found [24,25]. The formation of cyanides from DKP was suggested to proceed via the primary formation of imines. There are three suggested fragmentation modes for DKP that would produce imine [24,25] (Fig. 6). One of these is analogous to the reaction that forms imine from 2-azetidinone. It has been suggested that all cyclic amides would have similar decomposition modes, so that DKP as well as 2-pyridone would form HCN (for the non-aromatic DKP, via imine) as well as HNCO through reactions analogous to the reactions in Fig. 5 [20,21]. Furthermore, it was suggested that for all cyclic amides, the activation energy for the HNCO forming reaction would be lower than

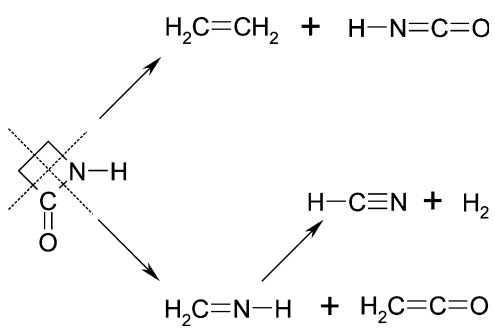

Fig. 5. Thermal decomposition reactions of 2-azetidinone [23].

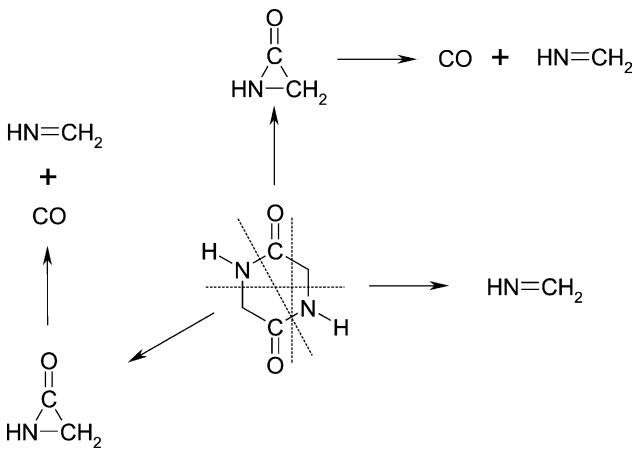

Fig. 6. Suggested pyrolysis reactions for DKP [24,25].

the activation energy for the HCN (or imine) forming reaction [20,21], as it is for 2-azetidinone. Schematically, the formation of nitrogen containing species from cyclic amides can be written as in Fig. 7.

Two of the suggested reactions in Fig. 6 produce two identical fragments each, both of which decompose to imine. The third suggested mechanism by which imine is thought to be formed produces one imine and a larger residual that contains a nitrogen atom. The HNCO formation is not yet known, but is likely to form a residual that contains nitrogen as well. Both the HCN and the HNCO formation from DKP could give residuals that contain nitrogen and can produce HCN or HNCO. The reaction rates of the residuals from DKP, producing HCN and HNCO, are probably not the same as for the original DKP. However, for 2-pyridone, both reaction k_1 and k_2 give one nitrogen containing molecule and one residual that does not contain nitrogen. The HNCO/HCN ratio therefore equals k_1/k_2 for 2-pyridone. In Fig. 8, the HNCO/HCN ratios for DKP and 2-pyridone as functions of reactor temperature are shown. For 2-pyridone, k_1/k_2 can be fitted to this curve. According to this fit, the difference in activation energy for the two reactions is 120 kJ/mol. This is a substantially larger difference than was estimated for 2-azetidinone, but it confirms the idea that the reaction producing HNCO has a lower activation energy than the competing reaction that produces HCN.

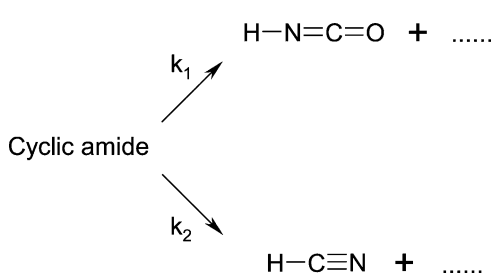

Fig. 7. Pyrolysis reactions for cyclic amides.

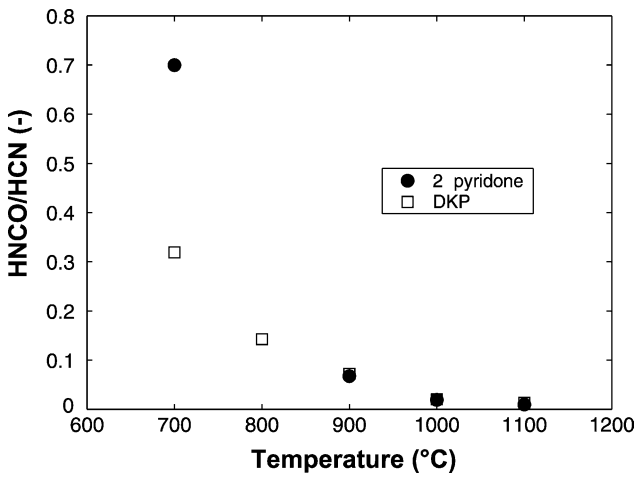

Fig. 8. HNCO/HCN ratios for 2-pyridone and DKP as functions of temperature.

3.1. Formation of HNCO from coal and coal tars

The pyrolysis of a solid fuel can be treated as a superposition of the pyrolysis of the fuel's different constituents. Biomass pyrolysis can be treated as the superposition of cellulose, hemicellulose, lignin and protein. For coal, no such clear separation of the fuel can be made. However, the coal consists of aromatic clusters bound together by weaker bridge bonds. Upon pyrolysis, the bridge bonds break and fragments of the coal are released as tars. The pyrolysis of the coal tars can be treated as the superposition of the clusters' different chemical functionalities.

In a novel work, a bituminous coal was pyrolysed at 600 °C [19]. The tars formed at 600 °C were then led to a second reactor where the tars were cracked at temperatures between 600 and 1000 °C. Some of the tars fed to the second reactor withstood even the highest temperature, but the light gases HCN, NH_3 and HNCO were also formed (Fig. 9). The presence of soot in the reactor was suggested to be a possible reaction route for NH_3 formation [19]. Speculated possible sources of the HNCO were 2-pyridone and 2-pyrrolinone. The fact that the yields of HNCO decreased with increasing temperature after 850 °C was suggested to indicate that HNCO decomposed at the higher temperatures.

The results in the above mentioned experimental study will be modelled under the assumptions that the nitrogen in the tars formed at 600 °C contain all of the nitrogen functionalities found in coal, and that the pyrolysis of the tar nitrogen can be treated as the superposition of pyrrole, amine/quaternary nitrogen, 2-pyridone and pyridine (Fig. 10). This is a simplification of the nitrogen structures in coal tars. Pyrrolic nitrogen can be in the form of pyrrole, indole, carbazole or larger ring clusters. The thermal decomposition of pyrrolic nitrogen will be influenced by the exact structure of the pyrrolic molecules. However, the decomposition rates for pyrrole and indole

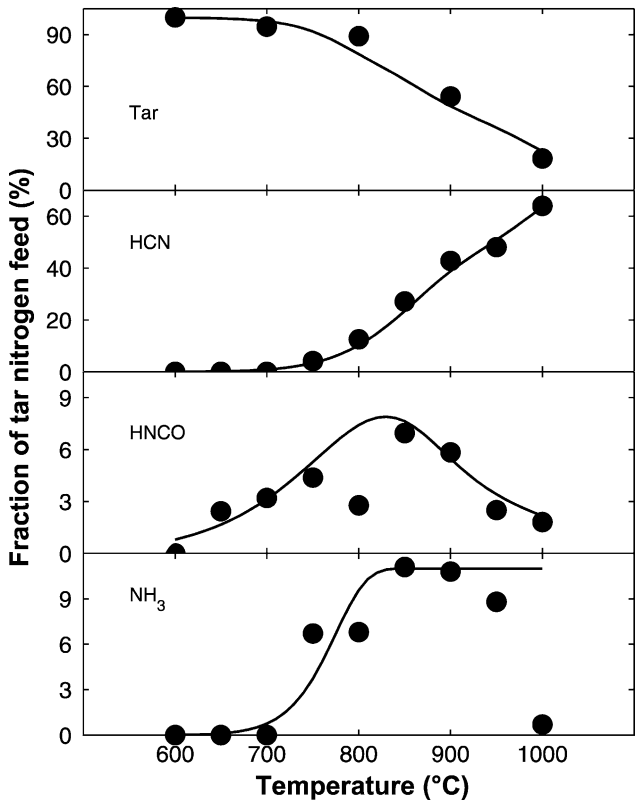

Fig. 9. Experimental (dots) yields of HCN, HNCO and NH_3 and the recovered amounts of tar nitrogen after cracking of coal tars [19]. The solid curves are the calculated yields (calculated residence time = 873/T), except for HNCO for which the line is the calculated curve multiplied by 5.

are not greatly different, and the same is true for the decomposition rates for the pyridinic molecules pyridine and quinoline [26]. For larger ring clusters, larger differences in decomposition rates can be expected. Pyrrole and pyridine thermally break down to HCN and nitriles [8,12]; see Fig. 10. As mentioned previously, calcium and other minerals might catalyse the reactions of pyrrole and pyridine. However, the volatilisation of minerals is negligible. This means that the pyrolysis of the tars is not affected by catalytic reactions of minerals. In the present study, 2-pyridone has been found to form HCN. At low temperatures, a high degree of HNCO is also formed from 2-pyridone. NH_3 is only formed in minor amounts from 2-pyridone, and this formation has been neglected in the modelling work herein. The NH_3 yields are here believed to be formed mainly from the fourth nitrogen functionality, whether it is amine or not, since conversion of quaternary nitrogen has been found to be directly correlated with NH_3 formation [1]. The maximum NH_3 yield from the tar pyrolysis was attained at 850 °C (Fig. 9), at which about 11% of the tar nitrogen was converted to NH_3 [19]. The fact that the NH_3 yield is decreasing at temperatures higher than 850 °C has two possible explanations. One would be that at high temperatures, a more dramatic decomposition of the aromatic amines/quaternary nitrogen than simple loss of NH_i side groups could produce HCN. The other possible reason is that at high temperatures, NH_3 has been found to decompose to nitrogen gas at catalytic surfaces [27]. The quartz frit in the reactor where the tars are being cracked or the soot formed at the highest temperatures might act as such a catalytic surface. A fact that favours the latter explanation is that for experiments at low temperatures, the nitrogen recovery (sum of tar nitrogen, HCN, HNCO and NH_3 but not N_2) was 97–114% of the original tar nitrogen, whereas at 1000 °C the nitrogen recovery was only about 86% [19] indicating that N_2 has been formed at 1000 °C.

The tars formed during primary pyrolysis were not analysed for nitrogen functionalities [19], which imposes an uncertainty in the comparison between experiment and

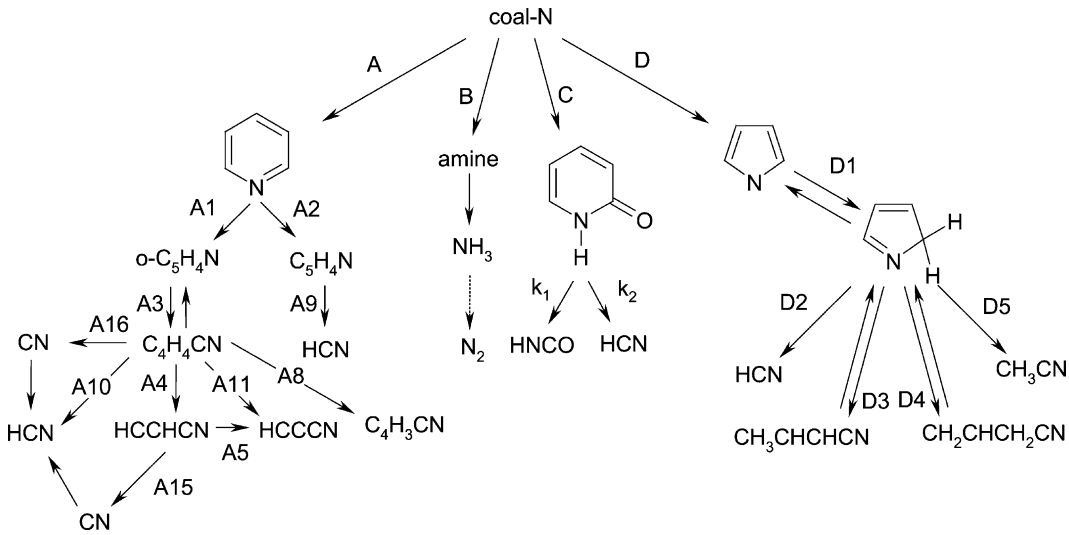

Fig. 10. The pyrolysis of coal-N leads to release of all nitrogen functionalities found in coal. Reaction A leads to pyridine, B to amine/quaternary nitrogen, C to 2-pyridone and D to pyrrole. The kinetics used to model the pyrrole and pyridine pyrolysis is taken from literature [8,12].

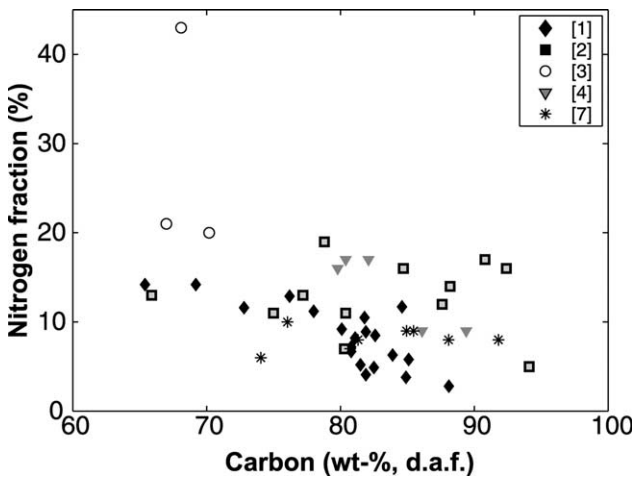

Fig. 11. Literature data on fractions of quaternary nitrogen [1–4] or amine nitrogen [7].

calculation. It is assumed here that the tar had approximately the same distribution of nitrogen functionalities as the parent coal. However, the nitrogen functionalities of the parent coal were not presented either [19], and the results from other studies have to be used instead. For a variety of coals with different rank, the amount of aromatic amines in the coal was 8 ± 2% from XANES measurements [7]. Literature data on quaternary nitrogen from XPS measurements show great variations (Fig. 11). The average amount of amine/quaternary nitrogen from Fig. 11 is 11%. The fraction of quaternary nitrogen is correlated with rank; but for coals with carbon content higher than 75% (for the coal from which the tars were derived, the carbon concentration was 83.2%), this correlation seems to be weak (Fig. 11). Catalytic decomposition of NH_3 is sensitive both to temperature and kind of catalytic material [27]. Since the same NH_3 yield (11%) was found at both 850 and 900 °C, and since this maximum yield was followed by a sharp decrease in NH_3 yield at higher temperatures, 11% is believed to be the ultimate NH_3 yield. The amine/quaternary fraction was therefore assumed to account for 11% of the tar nitrogen. The kinetics leading to NH_3 is modelled as a first order tar cracking reaction for the amine/quaternary nitrogen fraction of the tar. An Arrhenius type reaction constant with the activation energy 300 kJ/mol and pre-exponential factor 10^{15} s^{-1} was used to model the NH_3 yields (Fig. 9).

From XANES measurements, 58 ± 8% of coal nitrogen was pyrrole and 6–42% was pyridone [7]. XPS measurements showed that the fraction of pyrrole (+pyridone) was 44–80.2% [1–4]. The fraction of pyridine was 11 ± 9% [7], 7–40% [1–4]. The average values from the cited references are that 65% of the nitrogen is in pyrrole and pyridone structures, while 24% is in pyridine. The pyridine fraction in the tar can be better estimated from the degree of tar recovery at 1000 °C, since most of the tar nitrogen at this temperature originates from pyridine. At 1000 °C pyridone and quaternary nitrogen are completely decomposed, and only 2.5% of the pyrrole remains unreacted, while 15% of the original pyrrole has been converted into other tar products. At the same time only about 8% of the pyridine has been decomposed. Since the amount of recovered tars at 1000 °C is only about 18% of the original tar nitrogen, the pyridine fraction in the coal tars is probably less than the average in the coals (24%).

Based on the discussion above, the pyrolysis of the tar nitrogen was calculated, assuming that the tar nitrogen in Ref. [19] consisted of 11% amine/quaternary nitrogen, 20% 2-pyridone, 55% pyrrole and 14% pyridine.

The kinetics of pyrrole and pyridine decomposition is taken from literature [8,12]. Apart from pure pyrolysis reactions, a number of diatomic reactions are known to take place in the decomposition of pyrrole and pyridine. In the calculations presented in this work (Figs. 1 and 9), only the pyrolysis reactions have been considered (all shown in Fig. 10) since the gas composition in the cited experiments is unknown. However, for pyridine, the formation of CN radicals was considered to lead instantaneously to formation of HCN (Fig. 10). The calculations reveal that most of the pyridine remains unreacted after the pyrolysis at all temperatures. The pyrrole is almost unaffected by pyrolysis at low temperatures, but at high temperatures almost all of it is pyrolysed. Some of the pyrolysis products from pyrrole are nitriles with high boiling points (tars), but the main product is HCN.

At 600 °C, no light nitrogen containing gases were formed in the tar cracking experiments, indicating that all nitrogen functionalities were virtually unreacted. HNCO was formed at 650 °C. At this temperature neither HCN nor NH_3 was formed. This indicates that pyridone is the least thermally stable nitrogen functionality in the coal tars. The kinetics for 2-pyridone were based on the k_1/k_2 ratio found in the present work, and on the assumption that 1% of the pyridone was decomposed at 600 °C and 99% at 900 °C in the tar cracking experiments.

The results of the calculations are shown in Fig. 9. The calculated amounts of recovered tar and the HCN yields are very close to the experimental data from the tar cracking study [19] (Fig. 9). For HNCO the yield curves look qualitatively similar for experiments and calculations, but the experimental yields are about 5 times higher than the calculated ones. In Fig. 9, the calculated curve has been multiplied by 5 for comparison. It should be mentioned that the theoretical curve can be adjusted to give a better fit with the experimental one by changing the kinetic constants for k_1. However, it is not possible to get a perfect fit between the experimental and calculated curve, since the HNCO/HCN ratio for the tar cracking experiment at 900 °C is twice as high as it was in this study, despite the fact that HCN is formed from pyrrole as well as from pyridone in the tar cracking study [19]. Furthermore, the fact that HNCO but no HCN was found at 650 °C might be considered to contradict

the findings in this study. Extrapolating k_1/k_2 to 650 °C gives a predicted HNCO/HCN ratio of about 2. If 100% of the tar nitrogen was 2-pyridone, the calculated HNCO yields and the experimental HNCO yields from the tar cracking study would coincide, but this is an unlikely scenario and would not give a good correlation between calculated and experimental yields of HCN and NH_3 or of tar recovery.

It should be pointed out that the quantification of HNCO, both in the present study and in the tar cracking study [19], was done with HNCO spectra from other FTIR instruments than those used in the experiments. This can make the quantifications unreliable. For the tar cracking study, the HNCO calibration was taken from literature [28], which in turn was based on a FTIR spectrum from another work [29]. The calculated absorptivity [28] reveals that the calculation was based on a temperature of only 16 °C in the gas cell in the original work. The absorption in the original spectrum [29] was mistaken for the absorbance when the absorptivity was calculated [28]. This makes the calculated absorptivity from Ref. [28] incorrect. Furthermore, it is usually not possible to use absorptivities from one FTIR for another when different temperatures in the gas cells have been used. Usually, it is not even possible to use FTIR spectra from different kinds of instruments. This is shown in Fig. 12 for CO. In Fig. 12, the absorbance for 2740 ppm CO from FTIR2 is compared to the absorbance from a third FTIR (FTIR3) described elsewhere [20]. The *lc* product for FTIR2 was 0.968 times the *lc* product for FTIR3. Therefore, the absorbance from FTIR3 in Fig. 12 is multiplied by 0.968 for comparison. The curve for FTIR3 interpolates between the peak values. The peak values for both instruments should coincide if both instruments had the same absorptivity. Apparently, they do not. As mentioned in Section 2, the HNCO quantification made in this study is based on identical instruments, but nevertheless at high absorbances underestimates may occur. However, the absorbances for all experiments with 2-pyridone are

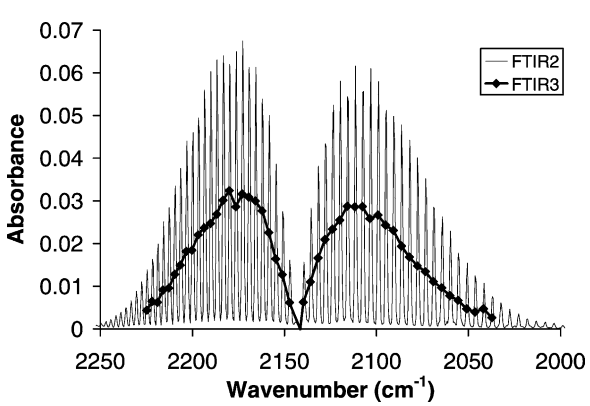

Fig. 12. Absorbance for CO from FTIR2 compared to the absorbance for CO (only peak values) from another FTIR (FTIR3) described in Ref. [20].

lower than the calibrated range for FTIR2 and therefore considered reliable. The reported HNCO yields from pyrolysis of coal [18] and coal tars [19] are probably overestimates. Still, the results are interesting, since they show that the HNCO yield is at a maximum at 850 °C. The decrease in HNCO yield at temperatures higher than 850 °C in the tar cracking study appears to be an effect of the selectivity toward HCN formation at the expense of HNCO for pyridone at high temperatures and not, as previously thought [19], an effect of that HNCO decomposes at the highest temperatures.

3.2. Formation of nitrogen containing gases from proteins and DKP

For DKP, the selectivity toward HCN at the expense of HNCO is favoured by high temperatures, as it is for 2-azetidinone [23], for 2-pyridone and for proteins [21]. Comparing the HNCO/HCN ratio for DKP with the same ratio for the proteins used previously [21] reveals that less HNCO is formed from DKP than from the proteins, especially at the highest temperatures. The higher HNCO/HCN ratios from the protein experiments could be explained by the presence of other reactions than the cracking of cyclic amides that form HNCO. An alternative explanation is the effect of particle size in the experiments. The protein samples were much larger than the DKP samples, which lead to lower effective temperatures in the protein experiments. This second explanation is in line with the fact that the difference in HNCO/HCN ratio between proteins and DKP increases with increasing reactor temperature. At temperatures lower than 700 °C, cracking of DKP is slow [30] is the reason why most DKP formed inside the protein particles does not react until it reaches the reactor temperature if the reactor temperature is low. At 700 °C, the HNCO/HCN ratio for DKP is about the same as for proteins [21]. At temperatures higher than 700 °C, pyrolysis rates are high, so that DKP formed inside the protein particles can be completely pyrolysed before it leaves the particle and reach the reactor temperature. The HNCO/HCN ratio for the proteins at 1000 °C [21] is about the same as the HNCO/HCN ratio for DKP at 900 °C.

For proteins that do not form char-N at 700 and 800 °C, the NH_3 yields were much lower than the HCN yields [20], while the opposite was true for proteins that do form char-N at these temperatures [21]. For one of the proteins that do not form any char-N, poly-L-proline, the NH_3 yield was comparable to what was found for DKP. This supports the hypothesis that the pyrolysis of proteins that do not form char proceeds via the primary formation of DKP. However, for another protein that does not form char-N, poly-L-leucine, the NH_3 yield was much higher than for DKP. Hence, there must be some other reaction that leads to NH_3 formation that does not cause char formation. The nature of this reaction is unknown at present. Nevertheless, it appears that proteins which form

high char-nitrogen yields also form a lot of NH_3, while proteins that form little char-N form more HCN. This latter formation most likely proceeds via cyclic amides such as DKP.

4. Conclusions

It has been verified that the cyclic amides DKP and 2-pyridone form both HNCO and HCN when pyrolysed. As for literature data on 2-azetidinone [23], the formation of HCN dominates over the formation of HNCO at high temperatures, while the opposite is true at low temperatures. NH_3 was also formed from both the amides, in yields corresponding to about 10% of the nitrogen content for DKP and about 3–4% for 2-pyridone. Both of the cyclic amides are 6-rings. The aromatic 2-pyridone is thermally more stable than the DKP. The results in this study support the idea that the HNCO formed from cracking of coal pyrolysis tars [19] originates from 2-pyridone or similar structures in the tar. It is also suggested that HNCO yields reported previously in literature may be overestimates. Furthermore, the results confirm that cracking of cyclic amides is an important source of the formation of HCN and HNCO from pyrolysis of proteins, and that most of the ammonia formed during pyrolysis of proteins originates from different reactions than the ones which lead to cyclic amides.

Acknowledgements

This work was financed by the Swedish Energy Administration and by the Centre for Combustion Science and Technology in Sweden (CECOST).

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