

Preparation of carbon dioxide adsorbents from the chemical activation of urea–formaldehyde and melamine–formaldehyde resins

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Abstract

Adsorption is considered to be one of the more promising technologies for the capture of CO₂ from flue gases. In general, nitrogen enrichment is reported to be effective in enhancing the specific adsorbent–adsorbate interaction for CO₂. Nitrogen enriched carbons were produced from urea–formaldehyde and melamine–formaldehyde resins polymerised in the presence of K₂CO₃ as a chemical activation agent, with activation undertaken over a range of temperatures. CO₂ adsorption capacity was determined to be dependent upon both textural properties and more importantly nitrogen functionality. Adsorbents capable of capturing above 8 wt.% CO₂ at 25 °C were produced from the chemical activation of urea–formaldehyde resin at 500 °C. Chemical activation seems to produce more effective adsorbents than CO₂ activation.

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1. Introduction

Increasing awareness of the influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO₂) emissions. In 2000, the burning of coal generated 37.8% of all CO₂ arising from fossil fuels [1] and as a result the strategy that is receiving the most attention involves the capture of CO₂ from large point sources (such as fossil fuel-fired power plants). The greenhouse gas can then be sequestered; stored underground or in the ocean over the long term. However, to economically sequester CO₂ it must be in a relatively pure high pressure form, requiring the capture and compression of the CO₂ emitted by the power plant.

The CO₂ capture step is projected to account for the majority (*ca.* 75%) of the expense for the overall carbon

capture and subsequent sequestration process. Aqueous solutions of amines have long been used by industry as absorbents for acid gas (CO₂, H₂S) removal, and in fact provide a large percentage of the natural gas sweetening operations. To date, all commercial CO₂ capture plants use similar processes based on chemical absorption with an aqueous alkanolamine solvent (*i.e.* Econamine FGSM, Kerr-McGee/ABB Lumus Crest MEA) [2–4] of which monoethanolamine is the most popular solvent [5]. However, regarding their application to flue gases, these technologies need significant modification and this ultimately leads to high capital and running costs. The typical energy penalty incurred by the operation of the MEA capture process is an estimated 15–37% of the net power output of the plant [6]. Therefore, although amine technology could be suitable for flue gases, with the prior SO_x and NO_x removal being essential, the development of alternative low cost technologies is crucial in the long term to provide a more cost and environmentally effective route to sequestering CO₂ on a global scale.

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Adsorption is considered to be one of the more promising technologies for the efficient capture of CO₂ from flue gases. Activated carbons are well known as adsorbents of gases and vapours [7]. Their specific application depends on the properties of the molecules to be removed/adsorbed. In the case of physical adsorption the sizes and volumes of pores are important, thus microporous carbons are used for the sorption/separation of light gases, whereas carbons with broad pore size distributions are applied for removal of toxins or other large organic molecules [7,8]. However, when specific interactions of adsorbate/adsorbents play a role in the adsorption process, other features of activated carbons, such as surface chemistry, should also be taken into consideration [8–10]. The surface chemistry of activated carbon is governed by the presence of heteroatoms such as oxygen and nitrogen. The nature of the heteroatoms is controlled by the chemical nature of the precursor and the method of carbon preparation and activation. The heteroatoms exist in the form of acidic, basic or neutral organic functional groups [9–11]. Moreover, delocalised π -electrons of aromatic rings and unsaturated valences also contribute to the basicity of carbonaceous sorbents [8].

Sometimes the original chemistry of the activated carbon surface is not sufficiently potent to enhance the specific adsorbate–adsorbent interactions or catalytic processes. In the case of CO₂ adsorption basic nitrogen functionalities are crucial for efficient CO₂ capture, which has led to efforts to maximise the number of nitrogen functional groups. Some of the most successful adsorbents for CO₂ have been developed via the alteration of the surface chemistry of porous substrates by impregnation with amine polymers, for example polyethylenimine [12,13]. Another method is the modification of the surface chemistry of the carbon matrix by the incorporation of heteroatoms such as nitrogen to enhance the specific adsorbate–adsorbent interaction. Nitrogen within the carbon matrix can cause an increase in the number of basic groups and changes the charge distribution in the graphene layers. Nitrogen incorporation has previously been demonstrated to enhance the adsorptive properties of activated carbons for hydrogen sulphide, SO_x, NO_x and acetaldehyde [14–17] and recently CO₂ [18]. However, there are few other studies dealing with the adsorption of CO₂ using active carbon, although there is great interest in technologies for controlling greenhouse gas emissions.

In this study, a suite of high nitrogen content carbon matrix adsorbents were prepared from the activation of urea–formaldehyde (UF) and melamine–formaldehyde (MF) resin, using K₂CO₃ as a chemical activation agent incorporated into the resin on polymerisation. It has previously been demonstrated that by the use of K₂CO₃ as an activation reagent, active carbons with high specific surface areas can be prepared [19–21]. By variation of activation temperature a range of adsorbents were prepared with adsorption capacities determined by thermogravimetric analysis.

2. Experimental

2.1. General materials and methods

All reagents and solvent used during this work were reagent grade and used without further purification.

2.2. Preparation of resins and activation procedure

UF resin was synthesised to include K₂CO₃ (1:1 ratio wt/wt) using the method of Hayashi *et al.* [20]. Briefly, for urea formaldehyde resin (UF) a mixture of, 18 g, K₂CO₃, 30 ml of formaldehyde (37 wt.% solution) and 15 g of urea was mixed in a beaker. The mixture was heated to 95 °C for 5 h whilst stirred. Based on the assumption that all of the urea is converted to UF resin a K₂CO₃ impregnation ratio of 1:1 is generated. The same procedure was used for the preparation of the melamine formaldehyde resin (MF) with a mixture of 33 g K₂CO₃, 21 g melamine and 20 ml formaldehyde. The resultant solid resins were cured for a week at room temperature and then placed in a vacuum oven for 24 h at 75 °C to ensure complete dryness, then powdered. Activation of the powdered resin was performed in a ceramic boat loaded into a stainless steel tubular reactor. Activation was undertaken at 400, 500, 600, and 700 °C for 1 h, after heating to temperature at 10 °C min^{−1}. A flow of 1 l min^{−1} of dry nitrogen was maintained throughout the activation process. After cooling, the char was recovered and washed with 0.1 M HCl and copious amounts of distilled water until the washings were neutral. The washed active carbon was dried at 110 °C under 100 mbar reduced pressure for 24 h. A reference sample of thermally activated UF resin was prepared by carbonisation at 400 °C for 1 h followed by activation for 0.5 h at 900 °C in CO₂, was generated for comparison. A commercial carbon (CC) specially oriented to CO₂ adsorption was also studied for comparison.

2.3. Characterisation of adsorbents

The organic carbon, hydrogen and nitrogen content of the UF and MF derived active carbon adsorbents were determined using a Thermo 1112 Series Flash EA. Oxygen content was determined by difference.

Textural characterisation was carried out using a ASAP 2010 with N₂ adsorption isotherms measured at −196 °C. The apparent surface area (S_{BET}) was evaluated by the BET equation [22]. The cumulative adsorption surface area (S_{BJH}) and pore volumes (V_{total}) in the pores ranging from 1.7 to 300 nm were calculated by the BJH method [23]. Mesoporosities were calculated from the ratio of S_{BJH} and S_{BET} . The average pore volume calculated from the equation $4V_{\text{total}}/S_{\text{BET}}$. Micropore (V_{micro}) and mesopore (V_{meso}) volumes were determined by means of the t -method [24].

2.4. CO₂ adsorption measurements

Assessment of the CO₂ adsorption and desorption potential of active carbons was determined using a Perkin Elmer, Pyris 1, thermogravimetric analyser (TGA). Temperature-programmed analysis was used to evaluate the influence on temperature upon the CO₂ adsorption capacity of the adsorbents. Temperature resolved CO₂ adsorption capacity was determined as follows: 10 mg of adsorbent was placed in an alumina crucible and heated to 100 °C in N₂ atmosphere at a flow rate of 20 ml min^{−1} and held isothermally for 30 min to remove any remaining moisture. The temperature was decreased to 25 °C and the gas switched to CO₂ with a flow rate of 20 ml min^{−1}. The sample was held isothermally at 25 °C for 2 h, and the weight increase measured used to derive the CO₂ adsorption capacity of the materials at room temperature. The temperature was then increased gradually at a rate of 0.25 °C min^{−1}, the slow heating rate allowing for equilibrium adsorption capacity to be attained, up to 100 °C, with the weight change of the adsorbent monitored to measure the adsorption capacity of the materials. After which the gas was switched to nitrogen whilst the temperature was maintained at 100 °C in order to study the desorption capacity of the adsorbents.

3. Results and discussion

3.1. Yields

Yields of the adsorbents after activation are presented in Table 1. These values are for the total recovered material that includes any remaining K₂CO₃ activation agent. Generally, product yield decreases with increasing activation temperature. In general higher yields were recovered from the UF as opposed to the MF derived carbons.

3.2. Elemental analysis

The chemical characteristics of the adsorbents are presented in Table 1. The unheated UF and MF resins have the expected elemental composition. Nitrogen contents are greater for the adsorbents prepared from the MF compared to the UF resin. Whilst this could be attributed to the higher initial nitrogen content of the MF resin, a far greater percentage of nitrogen is preserved upon activation, with the nitrogen contents remaining constant at approximately 30% after activation ($MF_{KC}^{500} - MF_{KC}^{700}$). The nitrogen content of the UF derived adsorbents decreases significantly with increasing activation temperature, with the adsorbent prepared at 700 °C having the lowest nitrogen content of all the adsorbent of 3.1 wt.%. As would be expected the percentage of carbon increases with increasing activation temperature. Whilst oxygen and hydrogen contents gradually decrease. Carbon contents of both MF and UF derived carbons (K₂CO₃ activation) increase linearly with activation temperature resulting in higher carbon contents of the UF carbons for each activation temperature. However, oxygen contents decrease with temperature for the UF carbon and slightly increase for MF derived carbons. Hydrogen contents for the MF adsorbents decrease linearly with activation temperature but, unexpectedly, UF carbons prepared at 600 °C and 700 °C have higher hydrogen contents than the unheated UF resin. N/C ratios are greatest for the precursor resins, and decrease with increasing activation temperature. The MF derived adsorbents have significantly higher N/C ratios for all activation temperatures in comparison to those derived from UF resin.

3.3. Textural properties

Table 2 presents the influence of carbonisation temperature on the textural properties of the active carbons. The non-activated resin samples have low surface areas, as

Table 1
Chemical characteristics and pyrolysis yields of the carbon materials studied

Sample	Resin	Activation reagent	Activation temperature (°C)	Product yield (wt.%)	N (wt.%)	C (wt.%)	H (wt.%)	O ^a (wt.%)	N/C atomic ratio
MF	Melamine–formaldehyde	–	–	–	48.5	30.1	3.9	17.5	1.61
MF _{KC} ⁵⁰⁰		K ₂ CO ₃	500	40.4	31.7	45.6	2.1	20.6	0.70
MF _{KC} ⁶⁰⁰			600	37.0	30.6	44.8	1.6	23.0	0.68
MF _{KC} ⁷⁰⁰			700	24.2	30.3	48.8	1.5	19.4	0.62
UF	Urea–formaldehyde	–	–	–	27.6	32.5	5.5	34.4	0.85
UF _{KC} ⁴⁰⁰		K ₂ CO ₃	400	42.9	12.3	57.5	3.3	26.9	0.21
UF _{KC} ⁵⁰⁰			500	40.4	10.4	64.3	5.0	20.3	0.16
UF _{KC} ⁶⁰⁰			600	39.7	8.5	72.0	6.2	13.3	0.12
UF _{KC} ⁷⁰⁰			700	35.2	3.1	77.1	6.3	13.5	0.04
UF _{CO₂} ⁹⁰⁰		CO ₂	900	12.5	10.6	80.5	0.4	8.5	0.10
CC		–	–	–	0.5	96.2	–	–	0.01

^a Calculated by difference.

Table 2
Textural properties of the carbon materials studied

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	BJH method ^a		Meso ^b	D_{BET} (nm) ^c	<i>t</i> -Method	
		S_{BJH} ($\text{m}^2 \text{g}^{-1}$)	V_{BJH} ($\text{cm}^3 \text{g}^{-1}$)			V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)
MF	4	2	0.042	0.45	4.08	0.002	0.039
MF _{KC} ⁵⁰⁰	12	7	0.012	0.54	7.55	0.005	0.007
MF _{KC} ⁶⁰⁰	23	22	0.082	0.93	8.84	0	0.06
MF _{KC} ⁷⁰⁰	56	16	0.104	0.28	4.54	0.018	0.047
UF	5	3	0.013	0.50	3.59		
UF _{KC} ⁴⁰⁰	25	13	0.041	0.54	9.27	0.004	0.03
UF _{KC} ⁵⁰⁰	365	75	0.109	0.21	6.35	0.145	0.067
UF _{KC} ⁶⁰⁰	910	178	0.400	0.20	4.97	0.401	0.087
UF _{KC} ⁷⁰⁰	2479	1283	0.952	0.52	3.85	1.073	0.253
UF _{CO₂} ⁹⁰⁰	444	184	0.230	0.41	1.80	0.171	0.110
CC	1225	683	0.96	0.56	1.20	0.487	0.294

^a Cumulative adsorption surface area (S_{BJH}) and pore volume (V_{BJH}) calculated by the BJH method (pores 1.7–300 nm).

^b Mesoporosity is defined as the ratio of $S_{\text{BJH}}/S_{\text{BET}}$.

^c D_{BET} , average pore size calculated by $4V_{\text{TOTAL}}/S_{\text{BET}}$.

would be expected. The BET surface area for both the UF and MF derived carbons increase with activation temperature. However, whilst the UF resin develops increasingly greater surface areas, up to $2500 \text{ m}^2 \text{g}^{-1}$ at 700°C , activation does not lead to the formation of high surface materials from MF resin. The highest surface area achieved from the chemical activation of MF resin being $55 \text{ m}^2 \text{g}^{-1}$ at 700°C . Chemical activation of UF above 500°C results in the generation of greater surface areas compared to the adsorbent prepared by CO_2 activation at 900°C . Pore volumes, determined by the BJH method, increase with higher activation temperatures, for both the UF and MF derived adsorbents, whilst average pore sizes decrease with increasing activation temperature for UF carbons. Comparing the micropore and mesopore volumes (V_{micro} and V_{meso} , respectively) calculated by means of the *t*-method it can be pointed out that increasing activation temperature generates mainly microporosity in UF carbons while MF carbons are fundamentally mesoporous materials. MF derived adsorbents exhibit irregular textural development with respect to the activation temperature. There seems to be an inflection at 600°C above which microporosity would start to be developed for the MF carbons. Nevertheless, for UF carbons as activation temperature increases so does the development of microporosity. Overall the textural properties for the UF derived active carbons at the corresponding activation temperatures are similar to those determined previously [20].

3.4. CO_2 adsorption capacities

The CO_2 adsorption capacity versus temperature of the UF and MF derived adsorbents are presented in Fig. 1a and b, respectively. Adsorption capacity is expressed as a percentage of the original mass of adsorbent and determined from the weight increase measured after the intro-

duction of CO_2 (wt.% = $\text{g CO}_2/100 \text{ g adsorbent}$). In all cases the highest adsorption capacity occurs at room temperature, after which capacity decreases with increasing temperature. The adsorption process is completely reversible, with all of the adsorbents returning to their initial mass after switching from the reactive gas, CO_2 , to non-reactive N_2 at 100°C .

Adsorption of CO_2 can be achieved by the use of either chemical or physical adsorbents. The interaction between the adsorbent and adsorbate for physical adsorption process is by relatively weak van der Waals forces. Predominantly physical adsorption is observed for the commercial carbon (CC) that has a negligible nitrogen content, and as a result CO_2 adsorption capacity decreases significantly at elevated temperature, falling by 75% between 25°C and 75°C (Fig. 1 and Table 3). Chemisorption results in the formation of a stronger chemical bond and previous results using polyethylenimine based chemical adsorbents have demonstrated CO_2 adsorption capacity to be constant or increase with temperature [13]. The CO_2 adsorption capacity of the materials developed in this study display a hybrid adsorption between these two systems (Table 3), with a smaller percentage decrease in CO_2 capacity from 25°C and 75°C compared to that of the purely physical adsorbent (Fig. 1 and Table 3). The rate of decrease in adsorption capacity with temperature is also related to the temperature of activation, generally decreasing with activation temperature, this is most likely related to the nitrogen content or functionality and will be discussed later.

In all cases activation with K_2CO_3 significantly increases adsorption capacity when compared to that of the original resin polymer (Fig. 1). The best performing adsorbents were generated from the chemical activation of UF resin (Fig. 1a), with UF_{KC}⁵⁰⁰ having the highest CO_2 adsorption capacity of all, exceeding 8 wt.% at 25°C . A wide range of adsorption capacities are observed for the chemically

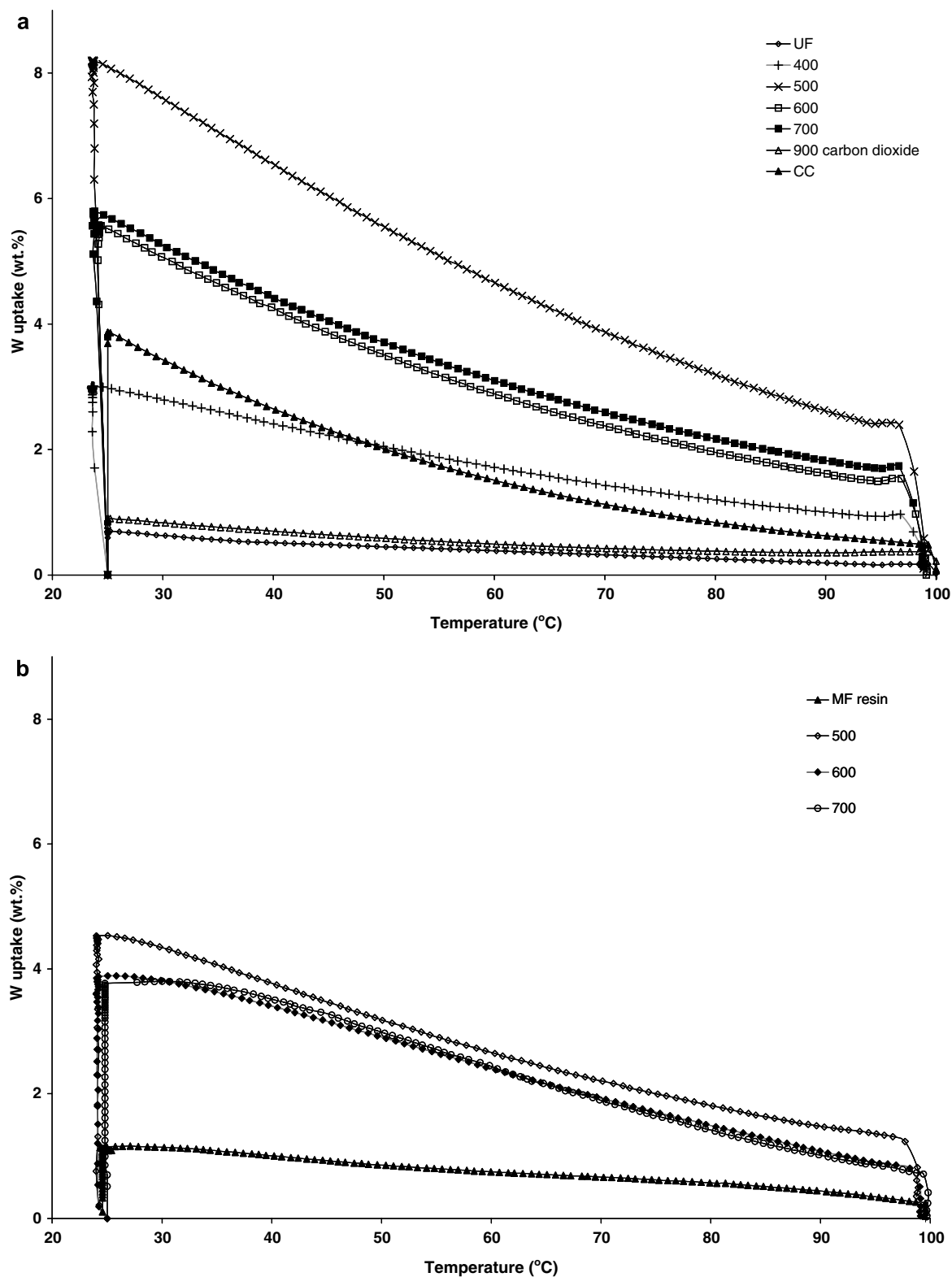


Fig. 1. Temperature-programmed adsorption/desorption profiles obtained by CO₂ saturation at room temperature followed by a heating (0.25 °C min⁻¹ from 25 to 100 °C) under CO₂, and finally, desorption in N₂ at 100 °C for (a) UF and (b) MF derived adsorbents.

activated UF resins at different activation temperatures. However, CO₂ adsorption capacity does not directly correlate with activation temperature. Whilst increasing the activation temperature from 400 to 500 °C (UF_{KC}⁴⁰⁰, UF_{KC}⁵⁰⁰)

results in increased capacity, higher activation temperatures (UF_{KC}⁶⁰⁰, UF_{KC}⁷⁰⁰) result in a reduction in adsorption performance. All adsorbent from the chemical activation of UF resin with K₂CO₃ have enhanced adsorption

Table 3
Change in adsorption capacity on increasing temperature from 25 °C to 75 °C

Sample	Adsorption capacity (wt.%)		Reduction in adsorption capacity (%)
	25 °C	75 °C	
MF	1.14	0.61	46.5
MF _{KC} ⁵⁰⁰	4.53	1.99	56.1
MF _{KC} ⁶⁰⁰	3.89	1.72	55.8
MF _{KC} ⁷⁰⁰	3.77	1.68	55.4
UF	0.70	0.35	50.0
UF _{KC} ⁴⁰⁰	3.01	1.31	56.5
UF _{KC} ⁵⁰⁰	8.19	3.57	56.4
UF _{KC} ⁶⁰⁰	5.57	2.20	60.5
UF _{KC} ⁷⁰⁰	5.80	2.30	60.3
UF _{CO₂} ⁹⁰⁰	0.90	0.38	57.8
CC	3.86	0.99	74.4

capacity when compared to the adsorbent prepared by CO₂ activation at 900 °C. The adsorption capacities of the MF derived carbons are generally lower than those achieved for the UF carbons at the same activation temperatures. For the MF adsorbents the highest CO₂ adsorption capacity exceeds 4 wt.% at room temperature (MF_{KC}⁵⁰⁰). Contrary to the UF adsorbents similar adsorption capacities were obtained for all three activation temperatures for the MF carbons (Fig. 1b).

The rate of CO₂ adsorption differs for the nitrogen enriched carbons prepared from chemical activation of UF and MF resins, as shown in Fig. 2. Equilibrium adsorption capacity at 25 °C is attained rapidly for the UF derived carbons, taking a maximum of 20 min from the introduction of CO₂ into the system. Adsorption is a much slower process for the MF derived active carbons, taking over 40 min to attain equilibrium. This could be as a result of the poor textural properties of the MF derived adsorbents (Table 2) limiting the rate of passage of CO₂ into the adsorbent. However, this could also be as a result of different nitrogen functional groups on the surface of the MF compared to the UF derived active carbons. The functional groups derived from the MF resin possessing higher activation energy of adsorption, limiting the rate of adsorption. This is detrimental to the applicability of the adsorbents to large scale processes where high gas flow rates and volumes are involved.

The adsorption of CO₂ is a combination of many factors, both physical and chemical, that will influence the performance of an adsorbent. Whilst textural properties will obviously influence the performance of an adsorbent, in the case of CO₂ adsorption chemical factors will also be significant. This is as a result of CO₂ being an acid gas, for which the efficiency of incorporation onto the surface of an adsorbent is dependent upon the presence of nitrogen functionality [18]. The dependence of the performance of the adsorbents upon activation temperature suggests that as well as a significant influence on the textural

properties, activation temperature greatly influences the surface chemistry of the adsorbents.

It is clearly evident that surface area is not the main determinant of the CO₂ adsorption potential of the active carbons. This is especially evident when comparing K₂CO₃ activated carbon (UF_{KC}⁵⁰⁰) to the CO₂ activated carbon (UF_{CO₂}⁹⁰⁰), where adsorbents with similar surface areas have significantly different CO₂ adsorptions capacities (Table 2 and Fig. 1b). Similarly, UF_{KC}⁶⁰⁰ and UF_{KC}⁷⁰⁰ have similar overall CO₂ adsorption potential, yet have significantly different surface areas, 910 m² g⁻¹ and 2479 m² g⁻¹ respectively. The influence of surface area and nitrogen content is further demonstrated in Fig. 3 where CO₂ adsorption capacities are normalised with respect to the BET surface area of the materials. Normalising the weight uptake during the temperature resolved CO₂ adsorption tests by the surface area of the adsorbent and the initial mass of the sample, gives a new parameter denoted W_s . This normalisation of the adsorption capacity reveals that the affinity of the surface towards the adsorption of CO₂ decreases with increasing activation temperature. This is evident for the UF resins for which a negative correlation between the temperature of activation and the amount of CO₂ adsorbed per m² is observed (Fig. 3). Therefore, the low adsorption capacity of UF_{KC}⁴⁰⁰ in Fig. 1 can be attributed to the poor textural properties developed during the low temperature activation. The same trend is observed for the active carbons prepared from the MF resin, with the adsorbent prepared at the lowest activation temperature (MF_{KC}⁵⁰⁰) having the highest adsorption capacity per unit of surface area. The MF derived adsorbents have a surface chemistry with a high affinity towards the adsorption of CO₂, even though the overall adsorption capacity is handicapped by the poorly developed textural properties of the adsorbent. The CO₂ adsorption capacity of the MF derived adsorbent per unit area is in some cases an order of magnitude greater than the UF derived adsorbents obtained at the same activation temperature (Fig. 3).

Further normalisation was performed to determine if the performance of the adsorbents is a result of the nitrogen content or the presence of different nitrogen functionalities with different basicities and therefore activity towards the adsorption of CO₂. Thus, the weight uptake during the temperature programmed CO₂ adsorption was normalised to the surface area, nitrogen content and the mass of the adsorbent, giving a new parameter $W_{S,N}$ (Fig. 4). As observed for the normalisation to surface area, the adsorbents activated at the lowest temperatures exhibit the greatest affinity towards the adsorption of CO₂, per unit of surface area and nitrogen. Normalisation to both surface area and nitrogen content reveals that the enhanced adsorption capacity of the MF derived adsorbents is not as a result of absolute nitrogen content. Different surface chemistry, more specifically nitrogen functional groups with greater basicity, must be present to account for the mass of CO₂ adsorbed per unit of surface area and nitrogen for the MF derived adsorbents greatly exceeding those of the UF resin.

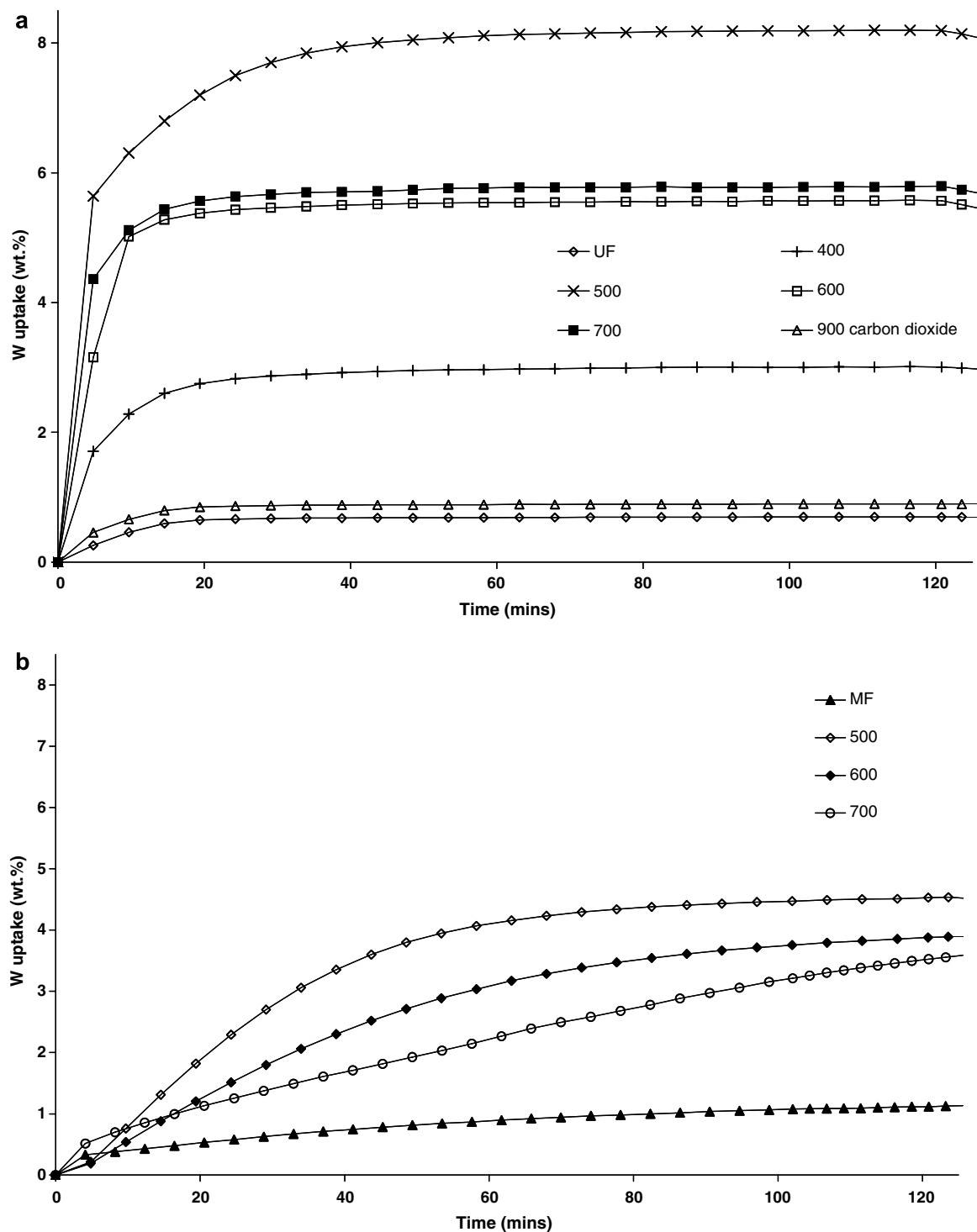


Fig. 2. Time resolved adsorption isotherms obtained by CO₂ saturation at room temperature for (a) UF and (b) MF derived adsorbents.

Melamine is known to undergo progressive condensation reactions on pyrolysis [25,26]. With increasing temperature the original functional groups of the melamine change from a mixture of amide and triazine ring nitrogen, undergo progressive condensation reactions and the elimination ammonia. This results in the formation of polymeric products called melam, melem and melon at 350, 450 and

600 °C, respectively. Melon is proposed to be composed of almost exclusively triazine ring structures, therefore dominantly pyridinic type groups. A similar process is proposed during the chemical activation of MF resin. With increasing activation temperature leading to the elimination of ammonia, resulting in an aromatic structure dominated by triazine rings above 600 °C. The formation of a

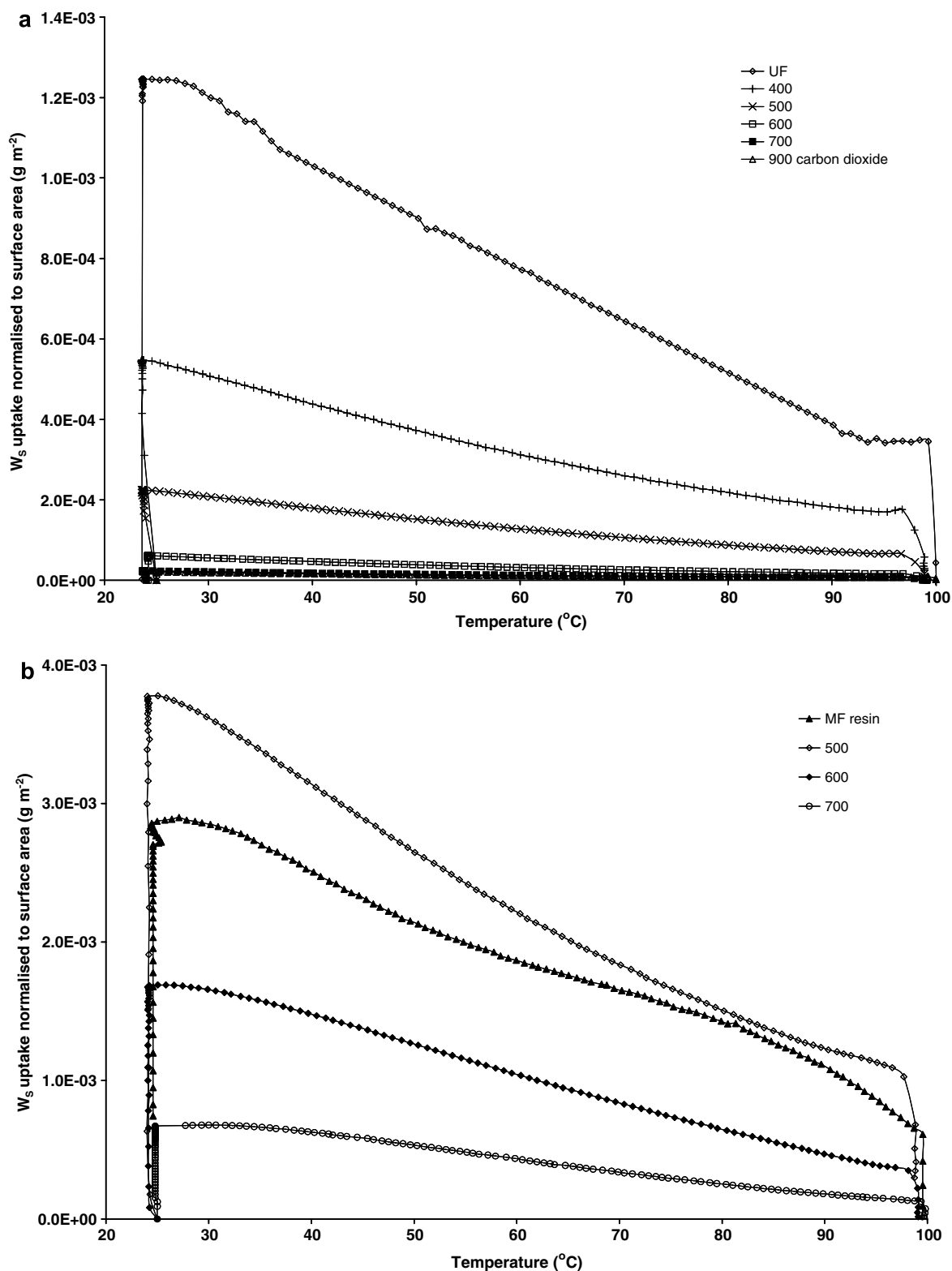


Fig. 3. Profiles for CO₂ uptake normalised by surface area during temperature-programmed CO₂ adsorption/desorption for (a) UF and (b) MF derived adsorbents.

structure dominated by thermostable triazine ring units accounts for the high and constant nitrogen content of the MF adsorbents on activation from 500 to 700 $^{\circ}\text{C}$.

Changes in the functional groups with temperature, with the elimination of amide groups and the formation of a condensed triazine dominated structure lead to a decrease

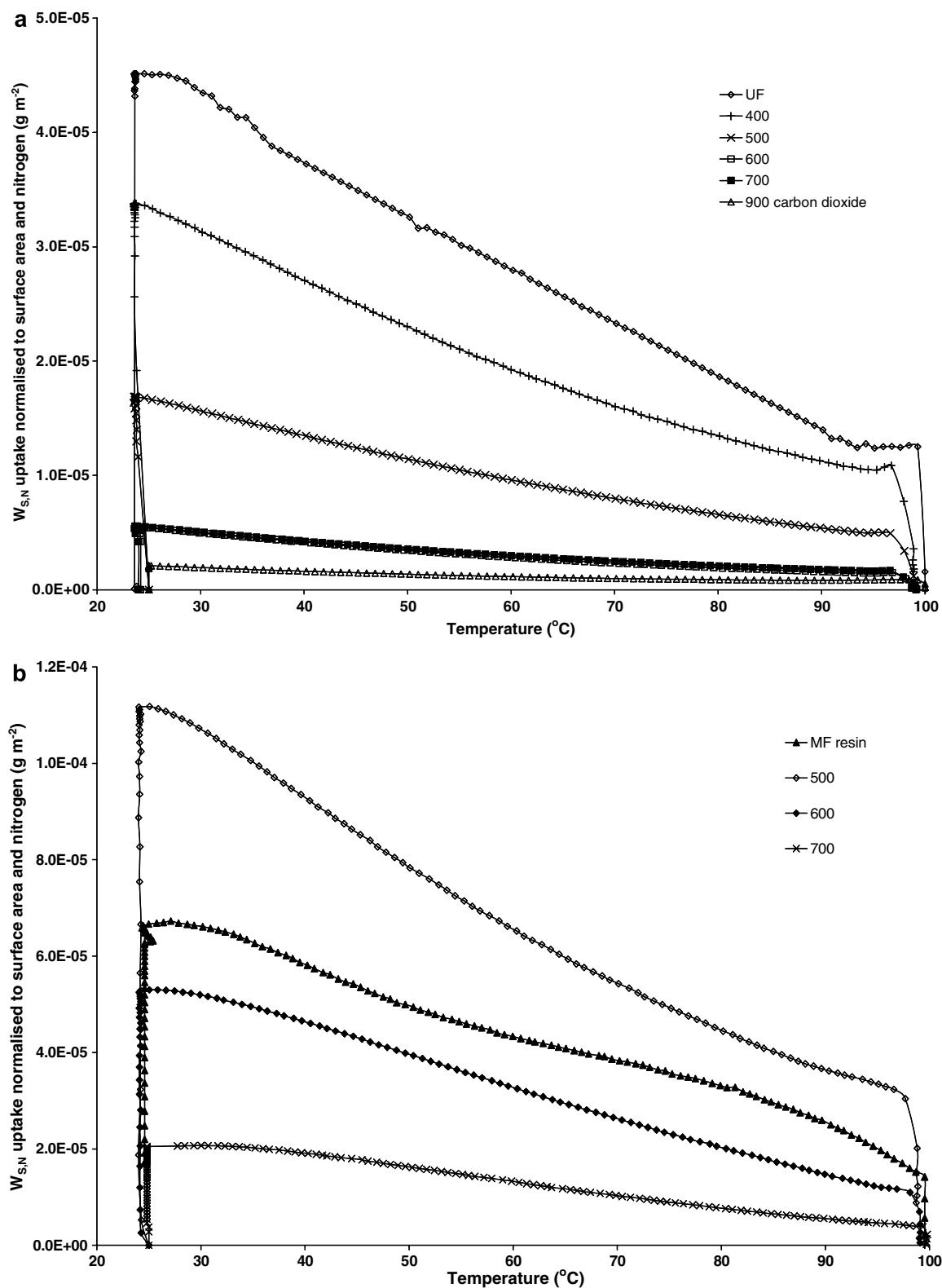


Fig. 4. Profiles for CO₂ uptake normalised by surface area and nitrogen content during temperature-programmed CO₂ adsorption/desorption for (a) UF and (b) MF derived adsorbents.

in the overall surface basicity of the adsorbent [27], which can be used to explain the decreased affinity of the surface of the MF derived adsorbents with increasing activation temperature.

The same principal can be applied to the decrease in the affinity of the surface of the UF derived adsorbent to CO₂. Adsorbents prepared at 400 and 500 $^{\circ}\text{C}$ from UF resin are likely to contain amides, i.e. free NH and NH₂, bonded

NH and NH_2 , and NH_4^+ species. These surface groups decompose at around 600 °C, and some nitrogen is converted into aromatic nitrogen species built into the carbon matrix [28,29]. Therefore, for the activation of UF resin above 600 °C the majority of the nitrogen incorporated into the carbon matrix is a component of six-membered polyaromatic structures. This evolution of the nitrogen functionalities with increasing activation temperature explains the decreasing affinity of the surface of the adsorbents to CO_2 with the functional groups capable of generating the most basic adsorbent surface [27], for example amine groups, eliminated by increased activation temperature, especially over 600 °C.

4. Conclusions

Effective CO_2 adsorbents have been generated from the chemical activation of UF and MF resins using K_2CO_3 . Moreover, carbons prepared by chemical activation seem to be highly effective for CO_2 adsorption compared to the one generated by physical activation with CO_2 . This would be dominantly as a result of the lower temperatures required to generate beneficial textural properties during chemical activation preserving higher nitrogen content in the form of more basic nitrogen.

Activation temperature has a strict control over both textural and surface chemistry of the adsorbents. Higher activation temperature results in a decrease in CO_2 adsorption capacity most probably because basic sites suitable for the adsorption of CO_2 are destroyed. However higher activation temperatures seem to generate more favourable textural properties for adsorption. This study also demonstrates the potential of the surface chemistry of melamine derived carbons for the generation of efficient CO_2 adsorbents, if their beneficial chemical properties could be combined with advantageous textural properties.

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