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**INVESTIGATION OF THE WETTABILITY OF
AMMONIUM NITRATE PRILLS**

by

Queenie Sau Man Kwok

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the
requirement for the degree of

Master of Science

Department of Chemistry

**Carleton University
Ottawa, Ontario
April, 2001**

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Chair, Department of Chemistry

Thesis Co-Supervisor

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ABSTRACT

ANFO, an admixture of ammonium nitrate (AN) prills with fuel oil, is widely used as a commercial explosive. The wettability of AN prills is one of the primary factors determining the physical stability and detonation behaviour of ANFO.

The wettability of various types of AN prills were compared using capillary penetration measurements where the penetration rates of various alkanes and fuel oil into packed columns of AN samples were determined. Comparisons were made with sessile drop contact angles on AN compressed discs. Complementary characterization studies using scanning electron microscopy (SEM), thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed to rationalise the observed differences in wettability.

The wettability of AN was found to be affected by several factors, including surface tension, viscosity, density, purity, polarity and/or polarizability of liquid used, as well as surface composition, porosity, bulk density, particle size, moisture content and thermal history of the AN samples.

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LIST OF ABBREVIATIONS

A	cross-sectional area of the glass tube
E_a	activation energy/kJ mol ⁻¹
g	acceleration due to gravity/m ² s ⁻¹
h	height of liquid front/cm
H_{eq}	maximum height of liquid front at equilibrium/cm
k	rate constant/min ⁻¹
K	geometry factor/mm ⁵
M	mass of penetrated liquid/g
Δp	pressure difference across the vapour–liquid interface
r	capillary radius/mm
R	average pore radius/mm
R	Gas constant/J mol ⁻¹ K ⁻¹
t	time/min
T	temperature/°C or K
V	volume/m ³
w	wetting rate/g ² min ⁻¹
W	wettability/mJ m ⁻²
W_a	adhesion wettability/mJ m ⁻²
Z	pre-exponential factor/min ⁻¹
α	fractional transformation
β	constant

γ_c	critical surface tension of wetting/mJ m ⁻²
γ_{lv}	surface tension of liquid–vapour interface/mJ m ⁻²
γ_s	surface tension of solid/mJ m ⁻²
γ_{sl}	surface tension of solid–liquid interface/mJ m ⁻²
γ_{sv}	surface tension of solid–vapour interface/mJ m ⁻²
ε	porosity
μ	dipole moment/D
η	viscosity of liquid/mPa·s
θ	contact angle/°
π_{sv}	film pressure of adsorbed vapour on solid
ρ	density of liquid/g cm ⁻³
τ	transition time from inertial to viscous regime/min

CHAPTER 1: INTRODUCTION

1.1 General Background

The physical characterization of materials, both in terms of their bulk and their surface properties, is crucial in many areas of applied science. Measurement of the wetting between a liquid and the surface of a solid can be used to assess surface properties. ANFO, an admixture of ammonium nitrate (AN) prills with fuel oil, is widely used as a commercial explosive. The wettability of AN prills is one of the primary factors determining the physical stability and detonation behaviour of ANFO. However, few AN wettability studies have been undertaken to date. This research explores the effects of several factors on the wettability of AN with a variety of organic liquids.

1.2 Ammonium Nitrate and ANFO

1.2.1 Ammonium Nitrate

Ammonium nitrate (AN, NH_4NO_3) is the most important commercial ammonium salt. AN has three widely recognized and very different uses: (i) as an agricultural fertilizer, (ii) as an ingredient of most commercial explosives, and (iii) as an ingredient for the production of nitrous oxide (laughing gas). In its pure form, AN is composed by mass of 60 % oxygen, 35 % nitrogen, and 5 % hydrogen.

AN is manufactured in many forms, including prills, dense flakes, granules, grained forms of solid, as well as a saturated aqueous AN solution. The AN prills fall into

two categories: (i) dense, agricultural-grade product, and (ii) low density, industrial-grade product.

AN is a readily available and relatively low-cost source of oxygen. It is stable enough at room temperature to be safely transported, stored and blended with other explosive components. Given these attributes, AN has been widely used as an essential ingredient in nearly all commercial explosives including dynamite, emulsions, and water gels. Recently, AN has also been considered as a potential effective oxidizer for rocket propellant and missile propulsion systems (Oommen and Jain, 1999; Mathew et al., 1999).

Despite the large-scale utilization of AN, the salt exhibits a number of undesirable properties. First, its extremely high solubility in water generally precludes its preparation through simple crystallization, as discussed by Doxsee and Francis (2000). Recrystallization of AN by slow evaporation of aqueous solutions affords poorly formed needle-like crystals (i.e. acicular forms or very slender prisms) with mother liquor trapped along their cores (Davey et al., 1989). Most commercial producers resort to prilling or related granulation processes, requiring subsequent drying and/or processing steps.

Secondly, AN is highly hygroscopic, and tends to agglomerate upon exposure to ambient temperatures and humidity, therefore compromising its effectiveness as an explosive. Additives and/or coating agents, such as dry clay (e.g. kaolinite and talc), are added to the AN prills to protect them from ambient humidity and to prevent agglomeration into a cake.

Figure 1.1. Phase transition of AN

Finally, as illustrated in Figure 1.1, AN has at least seven different solid state crystalline structures. The crystallographic data for phases I to V are summarized in Table 1.1 (Wyckoff, 1964; Hoden and Dickson, 1975; Lucas et al., 1979; Choi and Prask, 1983; Ahtee et al., 1983; Davey et al., 1989). Phases VI and VII were recently found by Shehap (1999) by infrared spectroscopy.

Besides the phase transitions between adjacent phases, a metastable phase transition II – IV can also occur at 50 °C, due to the close resemblance of the crystal structures in phases II and IV (Table 1.1). The state of the crystals has been shown to be closely dependent on the temperature, crystallization method, moisture content, purity and previous thermal history (e.g. Davey et al., 1989; Kestilä and Valkonen, 1994; van Driel et al., 1994).

There is abundant research and literature on the topic of AN phase transitions, analyzed by X-ray studies, optical and electron microscopy, Raman spectrophotometry, as well as Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA). However, there are wide discrepancies in the published results (transition temperatures, energies and reversibilities), and disparity over their interpretation.

Table 1.1. Crystallographic data of phases I to V of AN

Phase	Range of stability /°C	Crystal system	Density /g cm ⁻³	Crystal dimensions/nm		
				<i>a</i>	<i>b</i>	<i>c</i>
I	125 – 169.6	cubic	1.595	0.44	–	–
II	84 – 125	tetragonal	1.666	0.57	0.57	0.49
III	32 – 84	orthorhombic	1.661	0.77	0.58	0.72
IV	-18 – 32	orthorhombic	1.725	0.57	0.54	0.49
V	-170 – -18	tetragonal	1.725	0.80	0.80	0.98

The two phase transition temperatures at which cycling will occur under normal Canadian conditions are 32 °C and -18 °C when the prills are stored in rail cars or silos. The phase transition between phases IV and III is particularly problematic. As shown in Table 1.1, phase III has a completely different and “loose” packing mode of molecules in the crystal lattice (Wyckoff, 1964). The transitions of phase II and phase IV into phase III require more drastic changes of the crystal lattices (van Driel et al., 1994). Since significant solid-state reorganization occurs in the course of this phase transition, repeated cycling between phases IV and III leads to disintegration of AN, ultimately leading to powdering (Young, 1992).

In dry AN samples, the IV – II transition is generally dominant over the IV – III transition (Davey et al., 1989; van Driel et al., 1994; Kestilä et al., 1994). The IV – III phase change is catalyzed by water, and the percentage of IV – III transforming is highly dependent on the moisture content of the sample (Davey et al., 1989).

1.2.2 ANFO

For commercial explosives, AN prills are mainly used as a mixture with fuel oil, called ANFO. Due to the inexpensive and easily accessible ingredients of ANFO, as well as low sensitivity to mechanical and thermal stimuli, ANFO products have found extensive use in a wide variety of blasting applications, such as mining, quarrying, and construction.

A mixture of 94 mass % AN porous prill and 6 % liquid hydrocarbons (mostly, No. 2 diesel fuel) makes a practical and cost effective blasting agent. This optimum ratio provides the maximal theoretical energy, highest detonation velocity (Maranda et al., 1998), highest sensitivity, high efficiency and minimal post blasting toxic fumes (Rowland III and Mainiero, 2000). The ability of AN to adsorb liquid fuel is one of the primary factors determining the physical stability, detonation capability and detonation parameters of ANFO. Miyake and Ogawa (1998) have conducted a study on the detonation velocities of ANFO prepared by 6 mass % fuel oil and 94 mass % AN with different oil absorption capacity. Their results show that the detonation velocity of ANFO increases as the oil absorption capacity of AN increases. Similar results were also obtained by Maranda et al. (1998) from a comparison of the wettability of AN samples with oils.

Mader (1998) determined from both theoretical and experimental investigations that only 45 % of AN reacted at the detonation front of ANFO; the remaining 55 % AN behaved as inert and burned to complete reaction behind the detonation front. The detonation velocity increases with increase of the energy contribution of the chemical reaction to the detonation front. Thus, in order to obtain a higher detonation velocity, a

higher reaction rate, i.e. a better contact of the two components, is necessary. One significant method for obtaining a higher reaction rate is to improve the physical properties of AN. Thus the oil absorption capacity is a property of interest.

In earlier literature, Hong et al. (1991) have studied the wettability of AN by measuring the wetting enthalpy of fuel oil to powdered AN and the interfacial tension of the fuel oil and AN aqueous solution. They also determined that the wetting enthalpy increases and the liquid-solid interfacial energy decreases as the surfactant concentration increases. Thus, the wetting property of the fuel oil to AN could be improved by the addition of the surfactant.

In the explosives field, the wettability of other energetic materials has been studied using various methods (Dogan et al., 1999; Wu et al., 1997; Rivera and Matuszak, 1983; Palmer and Field, 1982; Elban, 1979). However, there is limited published information on the surface and interfacial properties of AN and fuel oil.

1.3 Wettability

Surface phenomena such as wetting are of considerable technical interest for many areas of applied science. Wetting processes have important applications in the fields of detergency, lubrication, flotation of minerals, wastewater treatment, oil recovery, and in pigment and particle technology. The major types of wetting mechanisms, which involve the interaction of a liquid with a solid, include adhesion, immersion, spreading, condensation, as well as penetration. The success of the wetting process is determined by the physicochemical surface properties of the interacting surface

components, and particularly the wettability and the surface tension (or surface free energy) of the components.

1.3.1 Definition

Wettability is defined in terms of the thermodynamic affinity of a solid surface for a liquid (Briant and Cuiec, 1972). Thus, the wettability is equated to the work exchanged by the system with its surroundings when the process of wetting for a given area of the solid surface is carried out reversibly.

For example, the wettability of adhesion (W_a), in which an adhesional union is formed between two pre-existing surfaces, is determined by the difference between the surface tension of the interfaces replaced, i.e. solid-vapour interface (γ_{sv}) and liquid-vapour (γ_{lv}), with the surface tension of the interfaces formed, i.e. solid-liquid (γ_{sl}) and:

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (1.1)$$

This represents the work required to create a unit area of the solid-liquid interface from a unit area of the solid-vapour and liquid-vapour interfaces. The wettability is also called the “specific wettability”, “wetting tension” or “work of wetting per unit area” (Kissa, 1996; Rouquerol et al., 1999).

The solid would wet spontaneously only if the wettability is positive. The various types of wetting do not all have the same contact angle requirement for spontaneous occurrence, and they may occur simultaneously (Jaycock and Parfitt, 1981).

1.3.2 Assessment of Wettability

Methods for measuring wettability can be broadly divided into qualitative and quantitative approaches. This distinction is based on whether or not the technique is capable of characterizing wettability in terms of surface tension. There are several strategies for quantitative assessment of the wettability of solid materials, in which the solid surface tension is determined by means of:

- (i) contact angle measured using direct or indirect methods (a review of the techniques are given in Section 1.4);
- (ii) enthalpy of immersion of a solid into a fluid measured using immersion microcalorimetry (Rouquerol et al., 1999);
- (iii) spreading pressure obtained by gas adsorption isotherms (Rouquerol et al., 1999);
- (iv) floatability of particles at liquid–fluid interfaces using film flotation technique (Fuerstenau and Williams, 1987);
- (v) suspension stability of dispersion of powders in liquids measured via sedimentation volumes (Vargha-Butler et al., 1985) or particle agglomeration (Omenyi et al., 1982);
- (vi) critical velocity of small particles at the solid–liquid interface of an advancing solidification (Li and Neumann, 1996);

Comparison between different techniques is not always straightforward, and they all have some limitations. For example, methods iv – vi are only applicable for samples in powder forms. Experimental difficulties may be encountered in the measurement of immersion enthalpy, due to the possible interference of the heat of dissolution and phase

transitions. Among the above methods, contact angle measurement is a simple and an economical approach to study the wettability of materials.

Other qualitative techniques, such as liquid–liquid contact angle measurement (Gerson et al., 1982), two-phase partition methods (Rosenberg et al, 1981), hydrophobic interaction chromatography (Magnusson et al., 1979) and salting-out aggregation tests (Lindahl et al., 1981) have also been applied to characterize the wettability of materials. However, they all suffer from the disadvantage that they are not able to express the data in terms of the surface tension of solid samples. They can only provide information as to whether one sample is more or less wettable than another.

1.4 Contact Angle

The contact angle (θ) of a liquid on a surface is an important aspect of the wetting properties of a system. The contact angle technique is widely used to evaluate surface characteristics such as wettability, hydrophobicity, and surface tension of solids.

1.4.1 Theory

Figure 1.2 illustrates the contact angle (θ) of a drop of liquid placed on a solid surface. The contact angle is formed at the vapour, liquid and solid interface, and is defined as the angle at the point of contact between the solid surface and the tangent to the surface of the drop. It is controlled by the surface tensions (or surface free energies) of the solid-vapour (γ_{sv}), the solid-liquid (γ_{sl}) and the liquid-vapour (γ_{lv}) interfaces. Their

Figure 1.2. Contact angle

relationship, for an ideal solid surface contacting a pure liquid, is governed by the Young equation (1855):

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1.2)$$

The contact angle is a result of the competition between the cohesive forces within the liquid and the adhesive forces between the liquid and solid. When the contact angle approaches zero, then the wettability is at its maximum, e.g. oil on Pyrex glass (Figure 1.3.a). If $\gamma_{sv} > \gamma_{sl}$, then $\cos \theta$ is positive, and the contact angle θ must be between 0 and 90°, e.g. water on Pyrex glass (Figure 1.3.b). If $\gamma_{sv} < \gamma_{sl}$, then $\cos \theta$ is < 0 and the contact angle must be between 90 and 180°, e.g. mercury on glass exhibits the highest angle (148°) commonly observed (Figure 1.3.c).

The contact angle decreases with increasing wettability, i.e. a low contact angle means high wettability and a high contact angle means poor wettability. All liquids wet all solid surfaces to some extent (i.e. no liquid gives a value of 180° for θ on any solid).

Figure 1.3. Different contact angle of liquids on a Pyrex glass surface

In general, a liquid is said to completely wet a solid if $\theta = 0^\circ$ and does not wet a solid if $\theta > 90^\circ$.

Note that in Eq. (1.2) the phases are mutually in equilibrium. The solid surface must be in equilibrium with the saturated vapour pressure. There must therefore be a film pressure of adsorbed vapour on solid:

$$\pi_{sv} = \gamma_s - \gamma_{sv} \quad (1.3)$$

where γ_s is the surface tension of solid. Thus

$$\gamma_{lv} \cos \theta = \gamma_s - \gamma_{sl} - \pi_{sv} \quad (1.4)$$

If $\gamma_{lv} > \gamma_s$ and the adsorption of the solid-vapour is assumed to be negligible, this implies $\gamma_{sv} = \gamma_s$ and π_{sv} is neglected (Fowkes, 1964; Newmann, 1974).

1.4.2 Wettability and Surface Tension Determination

For the assessment of wettability from the contact angle, a favourable case is when a contact angle θ can be measured between the liquid and solid in equilibrium with the vapour, so that the Eq. (1.2) can be applied. Eq. (1.1) (page 7) can be rearranged to give:

$$W_a = \gamma_{lv} (\cos \theta + 1) \quad (1.5)$$

which allows for the derivation of the wettability simply from the contact angle and the surface tension of the liquid.

Additionally, contact angle measurements have been used to determine the critical surface tension of wetting (γ_c), i.e., the surface tension of a liquid which would just wet the solid surface completely. Liquids with surface tensions less than the critical value (i.e.

$\gamma_{lv} < \gamma_c$) are deemed to be perfectly wetting, and their contact angle on the surface is zero. For partially wetting liquids ($\gamma_{lv} > \gamma_c$), the contact angle and the liquid surface tension are related by the expression (Zisman, 1964):

$$\cos \theta = 1 - \beta[\gamma_{lv} - \gamma_c] \quad (1.6)$$

where β is a constant. Therefore, γ_c can be estimated at the point where $\cos \theta = 1$.

Alternatively, γ_c can be determined through the geometric mean relationship (Neumann and Spelt, 1996), in which the solid-liquid surface tension (γ_{sl}) can be represented as:

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}\gamma_{lv}} \quad (1.7)$$

Combining Eq. (1.2) and Eq. (1.7) gives a relationship between $\cos \theta$ and γ_{lv} :

$$\gamma_{lv}(\cos \theta + 1) = 2\sqrt{\gamma_{sv}\gamma_{lv}} \quad (1.8)$$

Thus, γ_c can be determined from the experimental contact angle of a series of liquids with known γ_{lv} .

Zisman (1964) stated that γ_c is an empirical parameter closely related to, but not necessarily equal to γ_{sv} . For a given solid surface, γ_{sv} is expected to be constant when vapour adsorption is negligible; however, if vapour adsorption of liquids does play a role, then γ_{sv} can be different from liquid to liquid for the same type of solid surface.

At present, contact angles have also been used to assess the surface tension of solids (γ_s). The two methods which are most frequently used are the “equation of state approach” (Neumann, 1974; Spelt et al., 1992; Spelt et al., 1996) and the “surface tension component approach” (Fowkes, 1964; van Oss, 1988; Good and van Oss, 1992). The former approach is based on an equation-of-state relation which has been shown to exist

from thermodynamics (Li and Neumann, 1994); the latter approach stipulates that γ_{sl} depends not only on γ_{lv} and γ_{sv} but also on the specific intermolecular forces.

Both approaches have obtained consistent solid surface tensions for low-energy solids (e.g. polymers) where $\gamma_{lv} > \gamma_s$ and π_{sv} can be assumed to be negligible, i.e., $\gamma_{sv} = \gamma_s$. Thus for a very limited number of cases, the value of γ_s can be obtained through a measurement of γ_c . However, the usefulness of both approaches is rather limited. This is especially the case when chemical interactions play a role (Balkenende et al., 1998).

The calculated γ_s and γ_{sl} values are used to interpret and to predict the wetting and adhesion properties in technically relevant systems. At present there is a wide range of indirect approaches for obtaining γ_s and γ_{sl} . The attractiveness of using contact angles to estimate the values is the relative ease with which contact angles can be measured on suitably prepared solid surfaces.

1.4.3 Contact Angle Measurements

The choice of method for measuring contact angles depends directly on the geometry of the system. For a flat plate, the most convenient method is the sessile drop technique, where the angle of contact of a liquid drop or a bubble on a solid surface is measured. Contact angle goniometry employs a microscope to view the angle directly (Bigelow et al., 1946; Gaudin, 1957; Johnson and Dettre, 1965; Adamson et al., 1970; Dionísio and Sotomayor, 2000). More sophisticated approaches involve a photograph or digital image of the droplet (Spelt et al., 1987; Li and Neumann, 1990; Duncan et al., 1995; Grundke et al. 1996; Prokop et al., 1996; Apel-Paz and Marmur, 1999). Sessile

drop methods can reliably determine the contact angle on a smooth, homogeneous, impermeable, and nondeformable surface, such as a large single crystal.

The capillary rise on a plate can also be used to obtain contact angles, by measuring the height and the meniscus on a partially immersed plate (Neumann and Renzow, 1969; Cain et al., 1983; Tamy et al., 1988; Kwok et al., 1994; Rouquerol et al., 1999).

Another type of method is based on measurements on a liquid drop, whose size exceeds the capillary length (diameter of several cm), deposited on a horizontal solid surface (Rondelez et al., 1990). Under these conditions, gravity forces dominate and the liquid takes the form of a pancake, whose height is related to the contact angle.

The Langmuir-Schaeffer technique (Langmuir and Schaeffer, 1937; Fort and Patterson, 1963) also involves direct measurement of the contact angle: a light beam is directed at the triple line and the orientation of the reflected beam is determined.

A patent published by Dumoulin et al. (1984) describes a measurement technique that models a drop on a flat surface as a convex mirror receiving a light beam. The contact angle may be calculated using the diameters of the reflected beam and the drop.

However, all the above techniques require the samples to be in the form of either a flat surface or a hollow cylinder, and are not applicable to powders and porous materials for contact angles measurements. Sessile drop methods have also been applied to compacts, i.e. compressed discs of powders (Buckton and Newton, 1986a; Rosilio et al., 1998; Prestidge and Tsatouhas, 2000). However, it is questionable whether such wettability measurements are representative of the particles.

First, if the contact angle is low, the testing liquid begins to penetrate the compact immediately and a contact angle cannot be measured with precision (Rosilio et al. 1998). Second, the surfaces of the compacts are rough and porous. The measured angles are often different from those on smooth surface (Rosilio et al. 1998). Finally, the compacting process causes extensive particle surface deformation, which may alter their surface energy and roughness, and has been shown to decrease the contact angle of powders (Buckton and Newton, 1986). Thus, an indirect approach to contact angle measurements involving the penetration of liquid into a packed particle bed has been developed.

1.5 Capillary Penetration Measurements

The capillary penetration technique, which is also commonly called the “wicking” method, is based on the rate of liquid penetration into packed beds of particles. The technique has been applied to determine the wetting characteristics of a variety of powders or porous materials, such as pharmaceutical products (Buckton and Newton, 1986; Rosilio et al., 1998; Prestidge and Tsatouhas, 2000), textile (Rhee et al., 1993), wood (Walinder and Gardner, 1999), clay (Bi et al., 1999; Lee et al., 2000), rocks (Grattoni et al., 1995; Mosquera et al., 2000), minerals (Subrahmanyam et al., 1996), coke (Patraboy and Kruus, 1989), coal (Tampy et al., 1988), ceramics (Li and Giese, 1994; Mullet et al., 1999) and polymers (Grundke et al., 1996; Tröger et al., 1998; Shi and Gardner, 2000).

1.5.1 Theory

The tendency of liquids to rise up capillary tubes (of narrow bore), is called capillary action and is a consequence of surface tension. The basic equation that describes the kinetics of penetration of liquids into powder or porous bodies was developed by Washburn (1921). Assuming a quasi-steady-state, the behaviour of the liquids as Newtonian with laminar flow, and neglecting inertia effects, the liquid flow through a capillary can be deduced through Poiseuille's law (1842), as:

$$\frac{dV}{dt} = \frac{\pi r^4}{8\eta} \frac{\Delta p}{h} \quad (1.9)$$

where dV is the volume change ($= \pi r^2 dh$), h is the height reached by the liquid front at time t , r is the capillary radius, η is the viscosity of the liquid, and Δp is the effective driving pressure (force).

The total effective pressure generally consists of three separate contributions, capillary pressure, hydrostatic pressure and an externally applied viscous pressure. In the derivation of the Washburn equation, the total effective driving force of the capillary rise is assumed to be only the capillary pressure, neglecting the hydrostatic pressure. For laboratory-scale samples, the capillaries are very small and only short height rises are measured; the gravity effect can thus be neglected compared to the capillary pressure. The Laplace equation of capillarity for a vertical capillary of circular cross-section predicts the capillary pressure to be:

$$\Delta p = \frac{2\gamma_{lv} \cos\theta}{r} \quad (1.10)$$

where γ_{lv} is the surface tension of the liquid.

Combining Eq. (1.9) and Eq. (1.10), Washburn (1921) obtained the following equation for the flow in a single linear capillary:

$$\frac{dh}{dt} = \frac{r\gamma_{lv} \cos \theta}{4\eta h} \quad (1.11)$$

Eq. (1.11) neglects the effects of slip, gravity and inertial effects, and assumes there are no external pressure gradients. Integrating Eq. (1.11) with the boundary condition $h = 0$ at $t = 0$ gives:

$$h^2 = \frac{r\gamma_{lv} \cos \theta}{2\eta} t \quad (1.12)$$

For the capillary penetration of liquid in a column of packed particles, it has been assumed that the porous bed consisted of many small capillaries with an average radius R (e.g. Siebold et al., 1997):

$$h^2 = \frac{R\gamma_{lv} \cos \theta}{2\eta} t \quad (1.13)$$

In the case when the liquid front is not visible, or may not reflect accurately the inner progression of the liquid in the powder packing, the difficulties can be overcome by using the mass gain measurements (Kilau and Pahlman, 1987; Varadaraj et al., 1994; Grundle et al., 1996; Siebold et al., 1997). Eq. (1.12) can be modified by replacing h by the mass (M) of the liquid which penetrates into the capillary system:

$$M = \varepsilon \rho h A \quad (1.14)$$

where ε is the porosity of the packed powder column (calculated from the volume of all pores and the volume of the entire sample), ρ is the density of the liquid, and A is the cross-sectional area of the glass tube. Combining Eq. (1.13) and Eq. (1.14), the following is obtained:

$$M^2 = \frac{(R\epsilon^2 A^2)\rho^2 \gamma_{lv} \cos \theta}{2\eta} t \quad (1.15)$$

In the case of powder packing or porous solids, the geometry of the capillary system is unknown. The value of $(r\epsilon^2 A^2)$ in Eq. (1.15) is thus commonly replaced by an unknown geometric factor K , which leads to:

$$M^2 = \frac{K\rho^2 \gamma_{lv} \cos \theta}{2\eta} t \quad (1.16)$$

The capillary penetration measurements have been used to obtain information on the wettability of solid samples with a liquid (Grattoni et al., 1995; Bi et al., 1999), the contact angle (Rosilio et al., 1998; Prestidge and Tsatouhas, 2000), the surface tension of solids materials (Grundke et al., 1996; Tröger et al., 1998; Walinder and Gardner, 1999), as well as the porosity and pore radii of a pore network (Tampy et al., 1988; Li and Giese, 1994; Prestidge and Tsatouhas, 2000; Shi and Gardner, 2000).

1.5.2 Contact Angle Determination

In practise, the particle to be studied is packed into a glass tube, which is closed at its lower end by a filter. The filled columns are brought into contact with the testing liquid. The penetration rate of the liquid into the powders is determined either by the height of the liquid front or the mass gain as a function of time. In Eq. (1.13) and Eq. (1.16), γ_{lv} and η for different liquids are known parameters; h (or M) and t can be determined experimentally. Two unknown factors remain: R (or K) and $\cos \theta$. Both the terms R and K are empirical constants that depend only on the properties of the powder bed (such as porosity and void fraction).

Under the same particle packing conditions, R and K are approximately constant for columns packed with the same type of sample. They can be calculated using first a totally wetting liquid (so that $\gamma_{lv} < \gamma_{sv}$, and $\theta = 0$, then $\cos \theta = 1$). In most cases, alkanes are used, specifically heptane or octane due to their low viscosity and reasonably low vapour pressure. Knowing R or K , it is therefore very easy to derive the contact angle (θ) of non-wetting liquids ($0 < \theta < 90^\circ$).

The precise and accurate determination of R or K is critical and essential for the valid application of the Washburn equation. It was found that packing of particles is an essential point to obtain a reproducible geometry of the porous system (R or K). Therefore, a precise and consistent packing procedure is required to obtain constant and homogeneous powder packing.

1.5.3 Surface Tension Determination

Different approaches are available to determine the critical surface tension of wetting (γ_c) or solid surface tension (γ_s) by mean of penetration velocity data for a porous solid structure. One of the approaches is to follow the concept of determining the contact angle, and using Eqs. (1.6) or (1.8) for γ_c , or either the surface tension component or the equation of state approaches for γ_s (see Section 1.4.2).

Another strategy is to estimate the critical surface tension (γ_c) from a plot of normalized wetting rates as a function of the liquid surface tensions (γ_{lv}). By combining Eqs. (1.6) and (1.16), the normalized wetting rates is equal to:

$$\frac{2\eta}{\rho^2} \left[\frac{M^2}{t} \right] = K\gamma_{lv} (1 - \beta[\gamma_{lv} - \gamma_c]) \quad (1.17)$$

The plot shows a transition point when $\gamma_{lv} = \gamma_c$ (Prestidge, 2000). This method has also been used by Grundke et al. (1996), Tröger et al. (1998) and Prestidge et al. (2000) to determine the solid surface tension (γ_s); their results were in good agreement with literature values for a variety of materials.

Grundke et al. (1996) have shown that the capillary penetration of liquids into porous solids is related to the wetting tension. Thus, capillary penetration can determine the surface tension of solids with rough and porous surfaces. Furthermore, they used the solid surface tension to predict the contact angle of water; the results agreed with the contact angle observed on a smooth surface using direct measurement.

1.6 Research Objectives

The principal goal of the present research was to apply the capillary penetration measurements to determine the contact angle of ammonium nitrate prills with various hydrocarbons and fuel oil, and subsequently the wettability and surface tension of the ammonium nitrate prills from different sources. Comparisons are made with sessile drop contact angles on compressed discs of the same AN prills. Complementary characterization studies using scanning electron microscopy (SEM), thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed in an attempt to rationalise the observed differences in particle wettability. These studies were used to further develop the relationship between moisture content and crystalline structure change.

CHAPTER 2: EXPERIMENTAL

2.1 Materials

2.1.1 Ammonium Nitrate

Five samples of ammonium nitrate prills from three different categories were used in this study. They are identified as Types A – E. The samples were kindly donated by Orica Canada Inc., ETI Canada Inc., and the Canadian Explosives Research Laboratory. Their categories and prill size range are summarized in Table 2.1. The size ranges of the prills were determined by sorting the samples through sieves of various sizes. All the prills used in this study are commercial AN prills with additives and/or coating agents (e.g. kaolinite, talc). The type and the amount of additives and/or coating agents, as well as the previous thermal history of each individual sample is not known. Unless specified

Table 2.1. Characteristics of various AN prills

Type	Category	Prill size/mm
A	Porous	0.9 – 3.0
B	Porous	1.2 – 3.0
C	Porous	1.2 – 3.0
D	Mini	0.7 – 1.3
E	Dense	1.8 – 3.4

otherwise, the samples were used as received. All the prills were stored under identical conditions before measurements.

A reagent grade AN granule from J.T. Baker (Baker Analyzed A.C.S. Reagent 0729-05) was also used to prepare AN crystals and compacts (see Section 2.2). The reagent was used without further purification. The purity is claimed to be at least 99.5 %. However, the reagent may have a higher impurity, because the very hygroscopic nature of AN could have introduced significant water content.

2.1.2 Chemicals

A series of pure organic liquids was used as wetting liquids, as listed in Table 2.2. Except for fuel oil (diesel fuel), all other liquids were reagent grade with a purity of at least 98 %. The suppliers are listed in Table 2.2. The fuel oil was obtained from a local gas station, and the composition was analyzed by gas chromatography/mass spectrometer (GC-MS, see Section 2.8). All chemicals were used without further purification.

For the various wetting liquids, their surface tension (γ_{lv}), density (ρ) and viscosity (η) measured at 23 °C are listed in Table 2.2. The surface tension was measured using a CENCO-DuNOUY Interfacial Tensiometer (Central Scientific) and the viscosity with a Cannon-Fenske Routine Viscometer (Industrial Research Glassware Ltd.). The density was determined by weighing 10 mL of the corresponding liquids.

Additionally, a surfactant (Polyoxyethylene Sorbitan, SIGMA) was used; it was donated by Dr. Merv Fingas of Environment Canada. A mixture of heptane and the surfactant (approximately 0.5 %) was also used as a testing liquid. The viscosity, density and surface tension of this mixture have been confirmed to be the same as pure heptane.

Table 2.2. Data on the testing liquids at 23 °C

Liquids	Supplier*	$\gamma_{lv}/\text{mJ m}^{-2}$	$\rho/\text{g cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
Heptane	F	21.4	0.678	0.405
Octane	A	22.6	0.698	0.528
Nonane	A	23.4	0.715	0.687
Dodecane	A	26.4	0.747	1.403
Hexadecane	A	27.8	0.770	3.159
Toluene	C	31.5	0.862	0.572
Fuel oil	G	30.5	0.820	1.765

*Note: A, Aldrich Chemical Inc.; F, Fisher Scientific Co.; C, Cenco Instruments Co.; G, local gas station.

2.2 Sample Preparation

2.2.1 Crystals, Compacts and Powders

Because impurities influence the crystallization of AN (Sramko and Jona, 1985), high-purity material (reagent grade AN) was employed for crystals preparation. AN is highly soluble in water. At 20 °C, its solubility is 187 g in 100 g of water. A saturated solution of AN was prepared by dissolving excess AN in distilled water. Crystallization of AN crystals was conducted by slow evaporation of the saturated AN solution.

AN compacts of 5 mm in thickness and 13 mm in diameter were prepared for direct contact angle measurement. Samples (0.4 g) of Type A AN prills or AN reagent

were compacted in a Macro-Micro KBr Die (Aldrich Chemical Company, Inc.) at a pressure of 336 MPa for 5 min using a hydraulic press (Imperial Press Inc.).

Type A AN prills were ground to fine powder using an IKA model A10 analytical mill. Another AN powder sample was obtained by breaking down temperature-cycled prills (details for the temperature-cycled treatment are given in section 2.2.3).

2.2.2 Moisturized Prills

Moisturized AN prills were prepared by placing Type A prills under a bell jar with a pot of water. Samples with different moisture content were obtained by exposing the samples to water vapor for 1.5 to 24 hours. The relative humidity (R.H.) of air in the system was 70 – 80 % as measured by a humidity meter. The moisture content of each sample was verified using thermogravimetry (TG) (see Section 2.6).

2.2.3 Temperature-cycled Prills

Temperature-cycled prills were prepared by heat- and cold-treating Type A AN prills. The samples were first put into an oven (Fisher Scientific Co.) at 60 °C for 12 hours, then restored to room temperature for an hour, and finally placed in dry ice for 5 hours. This cycle was repeated twice.

Cold-treated prills were prepared by several different approaches: (i) placing the prills in dry ice (~ -78 °C) for 5 hours; (ii) storing the prills in a domestic freezer (~ -22 °C) for weeks; and (iii) keeping the prills isothermally at -30 °C for 5 hours using differential scanning calorimetry (DSC) equipment (see Section 2.7.1).

Two approaches were used to prepare heat-treated AN prills: by putting Type A prills in (i) an oven (Fisher Scientific Co.) at 60 °C for 12 hours, and (ii) a water bath (Lauda k-2/R Brinkmann Instrument) at 30 – 65 °C for 15 – 60 min.

2.3 Sessile Drop Contact Angle Measurement

A droplet of 5 μL of liquid was placed on the AN compact using a 5 μL micro-syringe (accuracy about 0.1 μL). The measurements were conducted using an optical microscope (America Optical Co.) with a glass reticule at the focal plane of the eyepiece (located within the microscope optical tube). The overall magnification was 50 $\times$. Every experiment was repeated; they were conducted at 23 ± 2 °C and R.H. of about 22 %. The low molecular weight hydrocarbons tend to evaporate under the light of the microscope. Therefore, all the measurements were taken within 2 min after placing the drops. All the sessile drop measurements were conducted at the Canadian Explosives Research Laboratory.

2.4 Capillary Penetration Measurements

The approach is based on measuring mass as a function of time of a liquid wicking up through a packed bed of particles contained in a tube. The experimental setup for a capillary penetration measurement is shown in Figure 2.1. About 5.0 g of AN samples are packed in a glass tube. The inner diameter and the length of the glass tube were 1.08 cm and 15 cm, respectively. The lower end of the tube was closed by a

Figure 2.1. Setup for capillary penetration technique

stainless steel filter, which was cut from a coffee filter. The column packed with samples was then dipped in a glass dish (volume of 50 mL and diameter of 10 cm) filled with the appropriate testing liquid. The penetration rate of the liquid into the samples was determined by monitoring the column mass gain as a function of time. Depending on the nature of both sample and liquid, an experiment took from 30 to 140 min.

An essential requirement for reproducible measurements is the uniform and reproducible packing of the tube with AN particles. The packing procedure was run as follows: the tube filled with the 5.0 g of sample was first dropped 20 times from a height of about 20 cm, and then was vibrated for 5 min with an electric vibrator (constructed from a shaver). The relationship between the vibration time and the height of the sample in the tube is represented in Figure 2.2. Since after 4 min, the height of the samples was constant, the time required to pack the tube was set at 5 min. Prior to each run, the

packing constant (bulk density) was calculated, to ensure a consistent packing for each type of sample.

Temperature as well as relative humidity in air near the column were recorded to make sure that their variations were limited, i.e., 23 ± 3 °C and 39 ± 18 % R.H. Although the variation of relative humidity was large in the whole duration of the study, it was noted that there is no significant difference in the results for the same sample at 21 and 60 % of R.H. All the capillary penetration measurements were conducted at Carleton University.

Figure 2.2. Sample heights in tube vs. vibration time for packing procedure

2.5 Scanning Electron Microscopy (SEM)

2.5.1 Structure Analysis

The external and internal structure of various AN prills were examined by a scanning electron microscope (SEM), model JSM 6400 (JEOL Ltd.) at the Department of Earth Science, Carleton University. The external structure of the prills was examined on unbroken prills, and the internal structure was observed in cleaved prills. These were prepared by cutting prills into halves with a sharp blade. The half having a smoother cleavage was chosen for examination. The samples were mounted on specimen studs using double-sided adhesive tape. Since AN is a non-conductor of electricity, the samples were coated with a gold-palladium alloy to prevent charging under electron bombardment. Gold-palladium alloy, which has a finer grain structure and a higher secondary electron yield, is the preferable coating for SEM imaging.

The AN samples were extremely sensitive to the electron beam, and disintegrated at high accelerating voltage. Therefore, the SEM observations were conducted at low accelerating voltage (3 or 8 kV) to minimize the beam damage to the samples. Generally, several observations and recordings were made on different prills of the same type at various magnifications from 30× to 5000×.

2.5.2 X-ray Microanalysis

An X-ray spectrometer attached to the SEM was used to chemically analyze small selected areas of various AN prills. The spectrometer is of an energy-dispersive (ED) type. Surface analysis was carried out by irradiating the samples with monoenergetic soft

X-rays and analyzing the energy emitted by electrons. Aluminium $K\alpha$ X-rays were used as an X-ray source in a vacuum of 1×10^{-9} Torr. A qualitative analysis of the surface compositions was performed by identifying the elements from their photon energies. No quantitative analysis was conducted; however, the approximate relative amount of each elements were determined by comparing the intensities of the responses.

For the X-ray microanalysis, the specimen studs mounted with samples were coated with carbon, which is the preferred coating element for X-ray analysis as carbon has a minimal effect on the X-ray spectrum. However, it is not ideal for SEM imaging, owing to its low secondary electron yield.

The detection limits of electron probe microanalysis are typically in the region of 50 ppm; hence, minor and trace elements are also able to be determined in many cases. However, the technique is only capable of detecting elements above atomic number 10, hence excluding H, He and Li.

2.6 Thermogravimetry (TG)

The water content of the as-received and as-prepared AN prills was established by a TA Instruments 2950 Thermogravimetry (TG) accompanied with a TA 5200 Thermal Analysis System at Canadian Explosives Research Laboratory. The sample was heated from 25 to 110 °C at 5 °C min⁻¹. A platinum pan containing about 30 mg of AN prills was purged with dry nitrogen at a flow rate of 60 mL min⁻¹ in the furnace and 40 mL min⁻¹ in the balance chamber. The moisture content was determined by the mass loss at 100

°C from the thermal curve, which gives the dependence of mass loss of the sample as a function of temperature or time.

To confirm the baseline of the TG, an experiment using the same heating profile was performed on an empty pan. The TG drift was $\sim 5 \mu\text{g}$, which represents 0.02 mass % for 20 – 30 mg of samples.

2.7 Differential Scanning Calorimetry (DSC)

A TA 2910 DSC module accompanied with a TA 5200 Thermal Analysis System (TA Instrument) was used to determine the phase transition temperatures for the AN prills studied. A Mechanical Cooling Unit (MCA) was used to obtain sub-ambient temperature. The system is located at the Canadian Explosives Research Laboratory. For the studies of the phase transitions, hermetically sealed aluminium pans containing about 5 mg samples were cycled between 150 °C and -70 °C (the lowest temperature reached by MCA) at 5 °C min⁻¹. The cell was purged with 50 mL min⁻¹ of nitrogen.

As mentioned in Section 2.2.5, DSC was one of the methods used to prepare cold-treated AN prills. The same DSC system described in the previous section was used. The experimental conditions were similar, except for the sample container and the heating profile. The samples were placed in open aluminium pans (without lids). An aluminium pan containing 10 mg of Type A prills was first cooled at 5 °C min⁻¹ from room temperature to -35 °C, and then kept isothermally at -35 °C for 5 hours. Finally, before removal from the cell, the samples were heated back to room temperature at 5 °C min⁻¹.

The reasons for the final heating step were to minimize the thermal shock to the sample, and to eliminate the possibility of condensation of atmosphere moisture on the prills.

2.8 Gas Chromatography and Mass Spectrometry (GC–MS)

The analysis of fuel oil was performed using Gas Chromatography/Mass Spectrometry (GC–MS) at Carleton University. A diluted sample of fuel oil was prepared by putting 8 μL of fuel oil into 10 mL of hexane. The analysis was carried out using a Varian 3400 – Saturn II GC–MS equipped with DB – 5 column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm film thickness; Chromatographic Specialists, J & W). The GC temperature program included an initial temperature of 70 $^{\circ}\text{C}$ and hold for 3 min, followed by 5 $^{\circ}\text{C min}^{-1}$ ramp to 230 $^{\circ}\text{C}$, followed by a second ramp of 15 $^{\circ}\text{C min}^{-1}$ to a final temperature of 280 $^{\circ}\text{C}$, which was held for 10 min. The conditions for the injection port include: an injection temperature of 280 $^{\circ}\text{C}$, and an injection volume of 2 μL . Detection was done using a mass selective detector with electron impact ionization set at a mass range of 50 to 650 amu.

CHAPTER 3: CRITICAL SURFACE TENSION OF WETTING

The assessment of the wettability of AN was performed using two different approaches to measure the contact angle and to determine the critical surface tension for wetting of AN with alkanes. One method measures the contact angles of liquids on a compact of particles; the other method measures the penetration of liquid into a packed particle bed. The results obtained from the two techniques are compared, and the validity of both methods is discussed.

3.1 Sessile Drop Measurements

3.1.1 *Contact Angles on AN Crystal*

The sessile drop method can provide reliable determination of contact angles of liquids on large single crystals. Hence, attempts were made to measure the contact angles of various liquids on AN crystals. However, crystallization of AN by slow evaporation of warm aqueous solutions afforded poorly formed needle-like crystals (i.e. acicular forms or very slender prisms). The needles tend to clump together upon exposure to air at ambient temperature. AN crystals were also prepared from supersaturated aqueous solutions at ambient temperature. The crystal growth was dominated by elongation along one axis. The resulting AN crystals form hollow tubes trapping mother liquor along their cores.

Earlier investigations (Davey et al., 1989; Doxsee and Francis, 2000) also reported similar difficulties in preparing AN crystals. Clearly, preparation of large AN

crystals is not simple. Hence, the sessile drop measurements were conducted on compacted AN prills.

3.1.2 Contact Angles on AN Pellets

The contact angles of sessile drops of liquids placed on the surface of compacted surfaces of AN prills and reagent grade AN crystals are listed in Table 3.1. The data presented are the average of two measurements. The uncertainty in each contact angle measurement is estimated to be within $\pm 3^\circ$. The measured surface tensions of the liquids (γ_{lv}) (see Section 2.1.2) and the literature values of the dipole moments (μ) of the liquids (Atkins, 1998) are also included in Table 3.1.

Table 3.1. Contact angles of different liquids on AN compacts

Liquids	$\gamma_{lv}/\text{mJ m}^{-2}$	μ/D	θ on compacted prills/ $^\circ$	θ on compacted crystals/ $^\circ$
Heptane	21.4	0	0	0
Octane	22.6	0	24	25
Nonane	23.4	0	27	29
Dodecane	26.4	0	33	33
Hexadecane	27.8	0	38	40
Heptane + surfactant*	21.4	—	0	0
Toluene	31.5	0.36	22	23
Fuel oil	30.5	—	24	24

Note: * polyoxyethylene sorbitan, approximately 0.5 %

X-ray microanalysis of the AN prills, which are presented later in Section 4.3, shows that the AN prill surfaces contain impurities (e.g. phosphorous and sulfur). To determine the effect of these impurities on the wettability of AN, the contact angle measurements were conducted on both compacted AN prills and reagent grade AN crystals. However, the results in Table 3.1 show that there are no significant differences between the two samples. Furthermore, no impurity was found on the surface of both samples from X-ray microanalysis (see Appendix III). The process of making pellets may have broken up the AN prills, exposing the prills' interior. This results in relatively less impurity, so that the pellet surface resembles that made from reagent grade AN crystals.

In Table 3.1, the sessile drop measurements on a series of alkanes show that the contact angle increased as the surface tension of the alkanes increased. The results seem to agree with the Young equation (Eq. 1.2), and also suggest that the surface tensions of the solid-vapour (γ_{sv}) and the solid-liquid (γ_{sl}) interfaces for alkanes with AN are similar.

The critical surface tension of wetting (γ_c) for AN with alkanes was determined using Eq. (1.8). In Figure 3.1, the values of $\gamma_{lv} (\cos \theta + 1)$ are plotted versus $\sqrt{\gamma_{lv}}$ of alkanes. From the slope of a linear regression, a value of $\gamma_c = 21.6 \pm 0.2 \text{ mJ m}^{-2}$ was obtained. The critical surface tension (γ_c) can be used to suggest a critical (maximum) value of γ_{lv} of liquid for complete wetting of the AN surface, assuming the liquid has similar properties as alkanes, e.g. polarity and polarizability.

As shown in Table 3.1, lower contact angles were obtained from toluene and fuel oil on AN pellet, while their liquid surface tensions (γ_{lv}) are higher than alkanes. The interactions between AN and toluene or fuel oil is different compared to alkanes, probably due to the difference in polarity and polarizability of the liquids.

Figure 3.1. Zisman plot for AN compacts with alkanes

As illustrated in Figure 3.2, the AN crystal structure is comprised of layers containing both NH_4^+ and NO_3^- ions. The attractive interaction between AN and a non-polar liquid arises from an ion-induced dipole interaction. The magnitude of this interaction is directly proportional to the polarizability of the liquid molecule. For alkanes, the bonds formed between C atoms are all sigma bonds, and the electron density is concentrated between the nuclei of the C atoms. On the other hand, the benzene molecule contains six electrons in the π delocalized molecular orbitals. The π electron densities are evenly distributed through the benzene molecule, and concentrate above and below the plane of the nuclei of the C atoms. Therefore, liquids containing the benzene

Figure 3.2. Illustration of AN surface with octane and toluene

group are more easily polarized by the NH_4^+ and NO_3^- ions than alkanes. They should thus have a stronger attraction to the AN surface. Toluene may also be attracted to AN surface through an ion-dipole interaction. For ionic solutions and polar liquids, a higher wettability with AN may also be the result of electrostatic, ion-dipole, and hydrogen-bond interactions with AN. Note that in Figure 3.2, the octane and toluene molecules may not lie flat on the AN surface, and may be oriented at an inclination to the surface.

Petroleum products such as diesel fuel contain a vast number of hydrocarbons, including many alkanes, cycloalkanes and aromatic compounds (Jüttner et al., 1995; Wang et al., 1995; Jennings et al., 1997). A GC-MS analysis of the fuel oil sample used was carried out (Appendix VI). The results show the presence of many compounds, including alkanes and aromatics. Each of the components has a different interaction with the AN surface. For example, the aromatic hydrocarbons in fuel oil have stronger interactions with AN than the alkanes, as shown by comparing the contact angle results for toluene and alkanes. To investigate the interaction of such a complex mixture with AN, sessile drop measurements utilizing each fuel oil component may be required.

The surface of the highly compacted particles seems flat and smooth; however, as observed from the SEM micrographs at high-magnification (Figure 3.3), the surface of

Figure 3.3. SEM micrographs of compacted AN (a) prills; (b) crystals

both pellet samples contain roughness or cracks. Surface roughness can affect contact angles; hence the results may differ from those measured on a smooth surface, i.e. a large crystal. Moreover, the compacting process may cause extensive particle surface deformation, which may alter the surface energy of AN and decrease the contact angle of the liquid. Consequently, contact angle measurements on a perfectly compacted surface may still not yield the same contact angle as the true original solid surface, i.e. the AN crystal surface. Since it is questionable whether the contact angle measurements on AN pellets are representative of the wettability of AN particles, the wettability of AN was further studied using the capillary penetration measurement as described in the next section.

3.2 Capillary Penetration Measurements

3.2.1 Wetting Rate Determination

A typical result obtained from a capillary rise measurement for an AN packed column is illustrated in Figure 3.4, where the square of mass gain (M^2) of the column is plotted versus time (t). All the results from capillary penetration measurements are attached as Appendix I.

According to the modified Washburn equation (Eq. 1.16), the mass gain (M) is predicted to be a square root function of the time. However, all the results obtained in this study show a parabolic increase of M^2 with time during the initial period. In some experiments, downward deviations from the straight line were also observed at longer times near the end of the runs. The non-linearities in the experimental M^2 vs. t

Figure 3.4. Capillary penetration results for AN prills with heptane

relationship may be due to the inappropriateness of the assumptions in the Washburn equation.

The effect of inertia is considered negligible, and laminar conditions are assumed to set up very rapidly in the Washburn equation. However, Quéré (1997) has shown that at the early stage, the capillary penetration is governed by inertial forces, and the transition time from an inertial to viscous regime is given by $\tau = \rho R^2 / 4\eta$. In this study, the initial unsteady state is observed for all the liquids tested, and the extent of this domain seems to depend on the liquid. However, the observed deviations do not agree with the above relationship of transition time. Apparently, the deviations at the early stage of the experiments may also depend on other factors, e.g. mass gain data may be affected by the liquid wicking on the internal wall of the glass tube.

Furthermore, the Washburn equation does not include the effect of gravity, which tends to decrease the forwarding of the liquid. An increasing height of the liquid front increases the influence of gravity, leading to a deviation of the experimental behaviour. According to Washburn (1921), the gravity effect can be neglected until $(H_{eq} - h)/h$ and the ratio H_{eq}/h differ by perhaps 10 %, i.e. $h \approx 0.1 H_{eq}$. Note that H_{eq} is the maximum height of the liquid front reached in infinite time, when capillary and hydrodynamic forces are equal at equilibrium. It is controlled by gravity (g), and is given by:

$$H_{eq} = \frac{2\gamma_{lv} \cos\theta}{R\rho g} \quad (3.1)$$

In this work, deviations were not observed in most of the experiments, in which the height of the penetrated liquid at the end of each run was usually < 4 cm. Small deviations downwards from the straight line were observed near the end of some experiments, which imply that gravity needs to be taken into account when the liquid height is higher.

Mass loss due to the evaporation of the adsorbed liquids on AN samples may also cause deviation from the Washburn equation. However, in this study, the samples were contained in a glass tubes and the liquid vapour can only escape from the system through the open end of the tube (see Figure 2.1). Since the vapour of the most volatile liquids could be re-adsorbed by the prills on the top, the evaporation effect of the testing liquid should be negligible.

In each experiment, the wetting rate (M^2/t) is estimated from the slope of a linear regression on the selected (M^2, t) data domain (Figure 3.4). This domain is selected from the region of the curve where its tangent has the least slope variation, i.e., where the effects of inertia and gravity seem to be negligible.

3.2.2 Wetting Rate of Various Liquids with AN

Capillary penetration measurements on Type A AN prills were conducted with various testing liquids, including a series of alkanes and fuel oil. The average values of the wetting rates determined from two to three replicates are summarized in Table 3.2. The error term of the values represents one standard deviation determined from the repeated experiments. The measured surface tension (γ_{lv}), density (ρ) and viscosity (η) of the liquids (see Section 2.1.2) are also included in Table 3.2.

As compared in Table 3.2, the wetting rates of the alkanes decrease with increasing γ_{lv} , ρ and η of the liquids, in agreement with the Washburn equation.

Table 3.2. Capillary penetration results for Type A AN prills with various liquids

Liquids	$\gamma_{lv}/\text{mJ m}^{-2}$	$\rho/\text{g cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	10^3 Wetting rate $/\text{g}^2 \text{min}^{-1}$	$\theta/^\circ$
Heptane	21.4	0.678	0.405	2.83 ± 0.10	0^a
Octane	22.6	0.698	0.528	1.97 ± 0.18	36
Nonane	23.4	0.715	0.687	1.24 ± 0.04	52
Dodecane	26.4	0.747	1.403	0.70 ± 0.04	55
Hexadecane	27.8	0.770	3.159	0.42 ± 0.04	46
Heptane + surfactant ^b	21.4	0.678	0.405	2.81 ± 0.12	0^a
Fuel oil	30.5	0.820	1.765	1.16 ± 0.33	31

Note: ^a assumes heptane wets completely, i.e. $\theta = 0^\circ$.

^b polyoxyethylene sorbitan, approximately 0.5 %

However, the results also suggest that fuel oil has a higher wetting rate on AN, while its γ_{lv} , ρ and η are also higher than dodecane. Since fuel oil is a mixture of alkanes and aromatic hydrocarbons (Appendix IV), the higher wettability of fuel oil with AN may be due to the higher attractive interaction of some of its components with the AN surface, as discussed in Section 3.1.2.

On the other hand, a poorer reproducibility of wetting rates was also obtained from fuel oil (error $\pm 28\%$) than from alkanes (error $\pm 10\%$). The variations in the wetting rate data may be due to non-uniform and preferential penetration of fuel oil. As shown in Figure 3.5, non-linearity and discontinuity were observed from the capillary penetration results for AN prills and fuel oil. Each of the components has different penetration rate, and the composition of the fuel oil may vary as it rises. The poor reproducibility and variation in wetting rate indicate the potential problems during

Figure 3.5. Capillary penetration results for AN prills with fuel oil

wettability testing with mixtures. It is thus important to use pure probe liquids in the capillary penetration measurements.

The reproducibility of the measured wetting rates also depends on the efficiency of the consistent column packing, i.e. a constant tube cross-section, a consistent packing procedure and, on average, the same porous structures. With respect to particle size effects, it is desirable to use narrow size fractions of particles to minimize the variation in the efficiency of the column packing. Thus, Type A AN prills in a size range 1.68 – 2.00 mm were used in this series of experiments. Since a consistent and precise procedure was used to pack the sample (see Section 2.4), the geometry factor (K) is assumed to be constant for this series of experiments.

3.2.3 Contact Angle Determination

For the geometry factor (K), a value of $(3.88 \pm 0.14) 10^{-3} \text{ mm}^5$ was calculated using the wetting rate of heptane, assuming heptane can totally wet the solid surface (i.e. $\theta = 0^\circ$ and $\cos \theta = 1$). The contact angles for AN prills with other testing liquids were determined from Eq. (1.16), using the K value and the correspondent wetting rates. The results are listed in Table 3.2.

The contact angles of alkanes obtained were significantly different from those measured by sessile drop measurements (see Section 3.1.2), in which the contact angles depends on the γ_{lv} (Table 3.1). In Table 3.2, the contact angles do not increase with increasing surface tension of the alkanes, contrary to the Young equation (Eq. 1.2). There are several possible explanations for this observation.

Firstly, the prediction of the wetting rate proportionality with the contact angles is only valid for simple pore shapes. For shapes other than uniform circular tubes, different equivalent radii will govern the viscous resistance in Eq. (1.9) and capillary pressure in Eq. (1.10). Mason and Morrow (1991), and Wong et al. (1992) have shown that the capillary pressure is not proportional to the contact angle, in circular pores of non-uniform cross section (e.g. a cone) and in pores of non-circular and uniform cross section (e.g. rectangular prisms).

In the AN prills studied, the shapes of the pores are highly irregular, as observed by scanning electron microscopy (the results are presented later in Section 4.2). Consequently, the contact angle that the liquid makes with the AN surface must be constantly changing due to the irregular penetration through the pores. Secondly, heterogeneity of the surface composition and differences in surface roughness may also cause local variations of contact angle. This means the concept of a constant contact angle within a porous solid is not valid. In these cases, these contact angles cannot be used in conjunction with the Washburn equation (Eq. 1.16).

3.2.4 Critical Surface Tension Determination

Because the critical surface tension of wetting for AN with alkanes cannot be determined using the contact angles (the method mentioned in Section 3.1.2), an alternative method which requires no quantitative determination of the contact angles is used. In this method, the term $2\eta M^2/\tau\rho^2$, which equals $K\gamma_{lv}\cos\theta$ according to Eq. (1.16), is called the “normalized” wetting rate and is plotted against the liquid surface tension (γ_{lv}). At the point where there is a transition in the wetting rates data, the liquid surface

tension (γ_{lv}) is equal to the critical surface tension (γ_c) of wetting (Grundke et al., 1996; Troger et al. 1998; Prestidge et al. 2000). As shown in Figure 3.6, the plot of the normalized wetting rates for alkanes and fuel oil with AN prills versus the liquid surface tension shows a minimum at $24.5 \pm 1.0 \text{ mJ m}^{-2}$.

The critical surface tension has been shown to be independent of the pore geometry of porous materials, and correlates with the solid surface tension of the material from which the porous materials were made (Tröger et al. 1998). Therefore, the critical surface tension can still be used to suggest a critical (maximum) value of γ_{lv} for complete wetting of AN surface with liquids of similar polarity and polarizability. The effects of these two properties are discussed in Section 3.1.2.

The critical surface tension (γ_c) determined from the sessile drop technique ($21.6 \pm 0.2 \text{ mJ m}^{-2}$) is slightly lower than that obtained by the capillary penetration measurements ($24.5 \pm 1.0 \text{ mJ m}^{-2}$). As discussed earlier in Section 3.1.2, the sessile drop

Figure 3.6. Normalized wetting rate versus liquids surface tension

measurements on AN pellets may yield a different critical surface tension due to the microroughness, different surface composition and deformation on the compacted AN surface.

In the capillary penetration measurements, the packed particle bed certainly does not represent a flat and smooth solid surface. However, the particles or porous materials under investigation will ultimately be used in their uncompressed form. The derived values for γ_c from any capillary penetration measurements are believed to provide much more relevant information than direct contact angle measurements on imperfect solid surfaces.

3.2.5 Validity of the Washburn Equation

In the capillary penetration measurements, the basic equation used to describe the kinetics of penetration of liquids into powder or porous samples is the Washburn equation (Eq. 1.16), with the effect of gravity and inertia neglected. In this study, the capillary penetration results show that these two assumptions are generally valid in selected domains of the data. These effects only cause observable deviations of the wetting rates at the early and final stages of the experiments, as discussed in Section 3.2.1.

As shown by the inconsistency of contact angle determination (see Section 3.2.3), the main deficiency of the model derived from the Washburn equation is that only a single cylindrical capillary is used to characterize a complex porous network. If the packed sample is compared to a bundle of capillaries of different sizes, the rate of capillary rise is proportional to the radius; hence, the liquid is subjected to a competition between pores of different sizes. In the AN prills studied, the pore channels are

interconnected in a complex network, and the pores sizes and shapes are highly irregular. Thus, the Washburn equation for a simple bundle of uniform and cylindrical capillaries should not be valid. Hence, the method cannot properly predict the way the liquid fills the pores.

However, the effect of different pores size and shape may cancel out when different liquids are compared in the same medium packed in a similar manner, and the wetting rates of different liquids can be used as an empirical measure of the relative wettability of AN prills. Given its simplicity, the capillary penetration technique is a valuable alternative for comparing the wettability of the samples.

3.3 Summary

The critical surface tension of wetting (γ_c) for AN with alkanes was determined from the sessile drop and the capillary penetration measurements, and values of 21.6 ± 0.2 and $24.5 \pm 1.0 \text{ mJ m}^{-2}$ were obtained, respectively. The sessile drop measurements on AN pellets yield a different critical surface tension due to the microroughness, different surface composition and deformation of the compacted AN surface.

The critical surface tension (γ_c) can be used to suggest a critical (maximum) value of γ_{lv} of liquid for complete wetting of the AN surface. However, this value can only be applied to liquids with properties similar to alkanes. Liquids with higher polarity or polarizability can have a higher wettability with AN due to the attractive interaction involving both dispersive and non-dispersive forces. Moreover, in the capillary

penetration measurement, the wetting rate of AN also depends on factors such as the viscosity, density and purity of liquid.

The validity of the Washburn equation is also discussed. The main deficiency of the model derived from the Washburn equation is that only a single cylindrical capillary is used to characterize a complex porous network. Hence, the method cannot be used to predict the exact process of the liquid penetration in AN prills. However, given the simplicity of the capillary penetration technique, it can be used as a valuable alternative to estimate the wetting rate. The obtained wetting rates serve as an empirical measure to compare the relative wettability of various AN prills.

CHAPTER 4: FACTORS AFFECTING WETTABILITY OF AN PRILLS

4.1 Wettability of Various AN Prills

The wetting rates with heptane of the as-received AN prills were measured using the capillary penetration technique; they are summarised in Table 4.1. Such wetting rate data can be used as an empirical measure of the relative wettability of the AN samples, as discussed in Section 3.2.5.

As seen in Table 4.1, there are significant variations in the wettability of the various AN samples. Among the five samples, Type A AN prills have the highest wetting rate with heptane. For Types B and C prills, the wetting rates are similar, and lower than that for Type A prills by about 13 %. The wetting rates for Types D and E prills are much lower than those for porous prills (Types A–C); they are respectively 55 % and 75 %

Table 4.1. Wetting rate of various AN Prills with heptane

Type	10^3 Wetting rate/g ² min ⁻¹
A	2.68 ± 0.05
B	2.26 ± 0.22
C	2.39 ± 0.18
D	1.20 ± 0.15
E	0.67 ± 0.02

lower than that for Type A prills.

As discussed in Chapter 3, the wetting process for AN is a function of the solid and liquid characteristics, as well as the solid-fluid interactions. Since the wetting rates of the five samples were measured using the same wetting liquid, the variations in their wettability are mainly due to the differences in their characteristics. Factors affecting the wettability of the AN samples are explored in the following sections. These include porosity, surface composition, bulk density, particle size and size distribution, moisture content and temperature cycling.

4.2 Effect of Morphology and Porosity

Scanning Electron Microscopy (SEM) was used to determine the external and internal surface morphology for the various AN prills. Only representative micrographs are presented here. All the SEM micrographs are attached in Appendix II.

As presented in Figure 4.1, the external surfaces of Types A, B and C AN prills are not smooth, and they have a non-uniform distribution of pores over their external surface. Comparing the three porous prills (Figure 4.1.a–c), there are slight differences in their surface openings. Type A prill has a channelled pore structure (Figure 4.1.a). Types B and C have characteristic growth on the external surface that covers the pore structure (Figure 4.1.b and c).

As depicted in Figure 4.2.a, all the AN porous prills (Types A–C) have a central hollow internally. Their internal structure, as shown in high magnification micrographs Figures 4.3, indicate that there are differences in the particle shape. Type A prill has a

pore structure in which the grains are interconnected with themselves (Figure 4.3.a). Type B prill has an internal structure composed of nodular shape (spheroid) particles with an irregular distribution of pores (Figure 4.3.b), whereas Type C prill consists of oriented dendritic particles with channel pores (Figure 4.3.c). The SEM micrographs suggest that the external and internal pore sizes of porous prills range from 10 to 80 μm .

Typical SEM micrographs of Types D and E AN prills are also presented in Figures 4.1 – 4.3. The external morphology of Types D and E prills is shown as a highly dense structure with very few surface pores in Figure 4.1.d and e. For Types D and E prills, although the central hollow is distinctly formed (Figure 4.2.b and c), there are no channels linking it to the external surface. From the general internal micrographs of Types D and E prills (Figure 4.3.d and e), it can be observed that the prills have a continuous solid mass which is interrupted by a few discrete pores. The approximate maximum pore size for Types D and E prills are 8 and 10 μm , respectively.

Figure 4.1. SEM micrographs on the external surface of AN prills (all $\times 150$): (a) A; (b) B; (c) C; (d) D; (e) E.

Figure 4.2. SEM micrographs on the internal surface of AN prills: (a) A–C ($\times 35$); (b) D ($\times 70$); (c) E ($\times 30$).

Figure 4.3. SEM micrographs on the internal surface of AN prills (all $\times 150$): (a) A; (b) B; (c) C; (d) D; (e) E.

Both the external and internal surfaces of Types D and E prills are much finer than the porous prills (Types A–C). The pore sizes for Types A, B and C prills are 10 times larger than those for Types D and E prills. The relatively high porosity of Types A, B and C prills contribute to their enhanced wettability (see Table 4.1). Among the porous prills, Type A prills have the highest wettability which may be the result of a higher porosity. However, SEM is only able to sample surface pores within a small viewing area, and it is insufficient for evaluating the percentage of pore structure.

At present, there are various methods for characterizing porous materials; however, among these methods, only electron microscopy and mercury penetration are suitable to describe the pore size range of AN prills ($> 1 \mu\text{m}$). Mercury porosimetry has been shown to incorrectly assess the overall pore geometry and the distribution of pores in AN prills (Chattopadhyay et al., 1994). Nuclear magnetic resonance (NMR) microscopy (Chattopadhyay et al., 1994) and High-resolution thermogravimetry (HR-TG) (Kwok and Jones, 2001) have been applied to characterize the structural properties of porous AN prills. Further comparison of the three porous prills (Types A – C) may be carried out using these techniques.

4.3 Effect of Surface Composition

X-ray microanalysis was used to characterize the surface chemistry of the individual samples of AN prills. An example of the results from X-ray microanalysis are shown in Figure 4.4. All the results are included in Appendix III. Spectra of the AN samples contain signals due to the elements of carbon, nitrogen, oxygen, phosphorous, sulfur, aluminum, silicon and calcium. The signal of C was mainly from the carbon coating of the samples prior to the measurements. Elements H, He and Li are not detectable by the technique, since their atomic numbers are below 10.

No quantitative analysis was performed; however, the relative quantity of each element was determined by comparing the intensities of the lines. The results for the sample are summarized in Table 4.2; the elements are listed in the order from highest to the lowest intensities. Evidently, beside the major constituents of AN (oxygen and

Figure 4.4. X-ray microanalysis on Type A AN prill

nitrogen), some other elements are also present on the surface of the prills. It is not surprising to find these elements, because different coatings and additives (e.g. kaolinite, talc) are added to prevent the adsorption of moisture by AN.

The X-ray microanalysis results in Table 4.2 suggest that qualitatively, Types D and E prills seem to have less impurity on the surface. However, the amount of the impurity on these two prills may not necessarily be less than on the others, since a strong signal of phosphorous was obtained from Type E prills (see Appendix III). Additionally, since the surface chemistry was analyzed by a small spot X-ray microanalysis on a selected area of AN samples, the results may not be representative of the complete sample.

Table 4.2. X-ray surface analysis of various AN prills

Type	External surface	Internal surface
A	O, N, S, Al, Si, P	O
B	O, N, Ca, S, P, Al	O
C	O, N, S, Ca, Al	O
D	O, N, P	O
E	O, N, P	O, N, P

The internal surfaces of the cleaved AN prills were analyzed using X-ray microanalysis, with the option of “area scan”. The area analyzed was about 0.16 mm^2 , which was approximately 100 times larger than that for the external surface analysis, but the depth of samples analyzed was also lower. The results in Table 4.2 suggest that there may be less impurity on the internal surface of the prills. Moreover, there was no nitrogen detected from the internal surface of Types A–D prills. Apparently, oxygen occupies the most outer layer of cleaved surface of the prills.

Surface impurities affect surface wettability of AN prills. To determine the effect of coatings or additives on the wetting of AN prills, comparison of AN prills with and without coating is required. However, AN is very hygroscopic without the coating. Hence, it would be difficult to eliminate the effect of moisture (Section 4.6) and to obtain valid results from capillary penetration measurement. Alternatively, wettability studies on the coating and additives used per se may provide hints on their effects on the wettability of AN.

4.4 Effect of Bulk Density

The bulk density, void fraction and prill size distribution for various AN prills are summarized in Table 4.3. The bulk density, which was calculated using the sample mass and volume in the tubes for each capillary penetration measurement (see Section 2.4), refers to the density of the prills, including pores and inter-prill spaces. The void fraction was determined by the volume of octane added to a cylinder packed with AN prills. The size distribution of the samples was determined by sorting the prills through sieves with various sizes.

The bulk density of AN prills depends upon the shape of the prills, their prills density, the geometrical arrangement, as well as the void fraction. Theoretically, for uniform sized spheres, the void fraction varies from about 0.26 to 0.48 for different types

Table 4.3. Bulk density, void fraction and size distribution of various AN prills

Type	Bulk density /g cm ⁻³	Void fraction	Prill diameter/mm*				
			> 2.0	1.7 – 2.0	1.4 – 1.7	1.0 – 1.4	< 1.0
A	0.83 ± 0.01	0.48 ± 0.01	34 %	41 %	10 %	14 %	1 %
B	0.75 ± 0.01	0.55 ± 0.01	52 %	46 %	1 %	1 %	0
C	0.76 ± 0.01	0.52 ± 0.01	95 %	5 %	0	0	0
D	0.97 ± 0.01	0.43 ± 0.01	0	0	0	0	100 %
E	0.91 ± 0.01	0.43 ± 0.01	98 %	2 %	0	0	0

*Note: Values correspond to mass % of prills within the specified sizes range, which is expressed in mm.

of packing from 100 % rhombohedral to 100 % cubic. The void fractions of Types A, D and E prills fall within these two values, but towards the higher value because of random arrangement of the samples. Types B and C prills have a higher void fraction, which may resulted from the non-uniform spherical shape of the porous prills.

Among the porous prills, sample A has the lower void fraction and higher bulk density (Table 4.3), due to its wider distribution in prills size (Table 4.3). Type A prills have about 25 mass % prills with smaller size. As discussed by Dallavalle (1948), for a binary or multiple component system (of varied sizes of spherical particles), the smaller component can fit in the interstices of the larger component, hence increasing the bulk density. Systems of one size component are not amenable to as high a bulk density as are multiple component systems, and binary systems do not reduce the void space as much as three or more component systems.

The higher bulk density enhances the wettability of Type A prills, in comparison with Types B and C prills (Table 4.1), while they have similar surface and structural properties (Section 4.2). For Types D and E prills, the bulk density is higher than for Type A prills. However, their high bulk densities are due to their higher prill densities, i.e. low porosities, and as discussed earlier in Section 4.2, the low porosity of Types D and E prills are the limiting factors for their wettability.

4.5 Effect of Particle Size

The surface area available for adsorption is dependent upon the particle size of the samples. The specific surface area for spherically shaped particles is inversely

proportional to the particle diameters, and the surface area per unit volume increases very rapidly with a decrease in particle size, especially at smaller diameters. This results in a much larger surface area per unit volume of materials accessible for liquid adsorption.

To study the effect of particle size on wettability of AN prills, Type A prills were screened into four size ranges, and their wettability with heptane was determined using the capillary penetration measurements. As compared in Table 4.4, there are no significant differences in the wetting rates of the samples. The wettability of AN prills seems to be weakly dependent on the prill size in this limited range.

Table 4.4. Wetting rate of AN prills of different sizes with heptane

Prill size/mm	10^3 Wetting rate/g ² min ⁻¹
1.0 – 1.4	2.22 ± 0.16
1.4 – 1.7	2.65 ± 0.22
1.7 – 2.0	2.65 ± 0.26
2.0 – 3.0	2.61 ± 0.15

The effect of particle size was further studied by using AN samples in powder form. The first powder sample was ground from Type A AN prills, and the second one was obtained by breaking down temperature-cycled prills (details for the temperature-cycled prills are discussed later in Section 4.7).

For the powders, the wetting rate of heptane is fast, and it is difficult to precisely monitor the penetration rate. Consequently, the comparison of the wettability of prills and

Table 4.5. Wetting rate of AN prills and powders with hexadecane

Sample	10^3 Wetting rate/g ² min ⁻¹
Type A prills	0.42 ± 0.04
Ground powder	75 ± 8
T-cycled powder	214 ± 18

powders was conducted with the wetting rate of hexadecane, and the results are listed in Table 4.5.

The wetting rate of AN ground powder is about a factor of 180 greater than Type A prills. The wetting rate is further increased with the temperature-cycled broken powder (~ a factor of 500), which has the finer particle size. As shown in Table 4.6, the majority of the ground powder was between 250 – 600 μm , and for the temperature-cycled, it is between 125 – 250 μm . In Table 4.6, the particle size distribution for both samples were determined by sorting the powders through sieves with various sizes

Table 4.6. Particle size distribution of AN powders

Particles size/ μm	Ground/mass %	T-cycled/mass %
38 – 125	5.2	9.0
125 – 250	26.5	44.4
250 – 600	57.7	26.7
> 600	10.5	19.9

With finer particles, the total surface area of the samples for adsorption is higher. Hence, the wettability of AN increases as the particle size decreases. Finer powders have substantially higher wettability than AN in prills form. However, they also have a greater tendencies to absorb moisture and to cake, which prevents the adsorption of fuel oil. Moreover, X-ray microanalysis shows that the surfaces of the ground powders contain oxygen, nitrogen and sulfur (see Appendix III). Compared to Type A AN prills (Table 4.2), the ground powders have less impurity on their surface, since the prills' interior is exposed after grounding. The substantial increase in wetting rates may also be caused by the difference in surface composition. If AN prills could be ground immediately prior to the application, or if the prill is friable enough to break down during pneumatic loading, a substantially higher wetting rate may result.

4.6 Effect of Moisture

Studies were carried out on the effect of moisture content on the wettability of AN with alkanes. Moisturized AN prills were prepared by exposing Type A prills to water vapour for 1.5 to 24 hours, in a closed bell jar with relative humidity (R.H.) of 70 to 80 %. The correlation of the moisture content and the wettability of the AN prills is investigated using thermogravimetry (TG) for moisture content analysis and the capillary penetration technique for the wetting rate measurements.

4.6.1 Moisture Content of AN Prills

The moisture content of the as-received and moisturized prills was determined by measuring water desorption from the samples using thermogravimetry (TG). For the as-received Type A prills, no mass loss was observed up to 120 °C as shown in Figure 4.5. The decomposition of AN usually begins at the melting point (170 °C) and is complete at 210 °C. In Figure 4.5, the mass loss obtained between 120 and 200 °C may have resulted from the thermodesorption of the adsorbed water on the prill surface, as well as sublimation and decomposition of AN. Since this thermodesorption of the water may not be easily distinguished from the other events, the moisture contents of the as-received and moisturized prills were compared using the total mass loss at 100 °C.

A plot of typical TG results for moisture analysis on moisturized prills is illustrated in Figure 4.6. The TG desorption curves for water represent the mass loss

Figure 4.5. TG curve for as-received Type A AN prills. Solid line: mass; dashed line: derivative of mass with temperature.

Figure 4.6. Typical TG results for moisture content analysis. Solid line: mass; dashed line: derivative of mass with Temperature.

against temperature. They show two segments and inflection points which may be ascribed to succeeding stages of the desorption process. The two stages of desorption can be better illustrated with the derivative of mass with temperature in Figure 4.6. The two peaks in Figure 4.6 correspond to the water desorption from the surface and the pores of AN prills. Upon heating, the film of moisture on the external surface will be released first, then followed by the pore water in the prills.

The moisture contents of various AN prills moisturized under 70 – 80 % R.H. for 1.5, 3, 5, 6 and 12 hours are summarized in Table 4.7. The error terms represent one standard deviation obtained from at least two replicates. The moisture content is a function of the time exposed to water vapour and the R.H. in the system. For the AN prills exposed to water vapour for more than 18 hours, the samples were dissolved, since AN is hygroscopic and readily soluble in water.

Table 4.7. TG Results for moisture analysis of AN prills

Time of moisturizing/h	Moisture content/mass %
0	0
1.5	0.46 ± 0.03
3	2.18 ± 0.04
5	1.10 ± 0.10
6	2.42 ± 0.11
12	3.79 ± 0.13

4.6.2 Wettability of Moisturized AN Prills

The wetting rate of the various moisturized AN samples with heptane was determined using the capillary penetration technique. As shown in Figure 4.7, the results from the capillary rise measurement show that the wettability of AN prills decreases linearly with increasing moisture content.

The lower wettability may be caused by blockage of the pores and the surface of AN prills by water, or even by dissolving the prill surface, as shown in Figure 4.8 with a prill exposed to moist air for 12 h. Prills moisturized for a shorter period may not be seriously affected. However, the adsorbed water may still increase the hydrophilic property of AN prills, and increase the contact angle of AN with alkanes, thereby preventing the alkanes from entering the pores of AN prills.

Figure 4.7. Effect of moisture content on the wettability of AN prills. The error bars show standard deviation of at least 2 replicates.

Figure 4.8. SEM Micrograph of moisturized AN prill

4.7 Effect of Temperature Cycling

4.7.1 Disintegration of AN Prills

Pure AN crystals have several phase transitions (see Section 1.2.1). After cycling through these temperatures, AN prills may have a different volume and structure. The two temperatures at which cycling will occur under normal Canadian conditions are 32 and -18 °C when the prills are stored in rail cars or silos. Practical problems are observed when AN prills are cycled through these two phase transitions during transportation and storage.

To investigate the effect of temperature cycling on the wettability of AN prills, capillary penetration measurements of temperature-cycled prills were attempted. The temperature-cycled prills were prepared by heat- and cold-treating Type A AN prills. The samples were first placed into an oven at 60 °C for 12 hours, and then in dry ice (sublimation temperature -78 °C) for 5 hours.

As illustrated in Figure 4.9, the prills become very easy to degrade, ultimately leading to disintegration, or powdering after the temperature cycling. Capillary

Figure 4.9. SEM Micrograph of temperature-cycled prill

penetration measurements could not be performed with samples remaining in the prill form, because the temperature-cycled samples could not withstand normal handling, even with very gentle loading into the tube.

To further study the effect of temperature cycling on the disintegration of AN prills, differential scanning calorimetry (DSC) was used to determine the phase transitions temperature of the AN prills studied. Moreover, to identify the phase change (at -18°C , or 32°C , or combined) causing the disintegration, studies were also conducted on prills subjected only to either cold- or heat-treatments.

4.7.1.1 DSC Results for Phase Transitions of AN Prills

Figure 4.10 shows DSC traces obtained for the Type A AN prills. The plot indicates the monitored heat flow in and out of the sample against temperature while the temperature of the sample is ramped at $5^{\circ}\text{C min}^{-1}$ between -70 and 150°C . When the

Figure 4.10. DSC results for phase transitions of AN Prills

sample undergoes an exothermic reaction, heat will flow out from it; endothermic processes cause heat to flow into the sample.

Upon cooling, three phase transitions were observed at about 119, 44 and -34 °C. On heating, phase transitions occurred at -6, 52 and 125 °. As described in Section 1.2.1, AN has at least seven solid phases transitions at 125, 84, 32, -18, -34 and -50 °C (see Figure 1.1). On dry AN samples, it is commonly observed that a combined transition of IV – II and IV – III at 50 °C is dominant over the IV – III transition at 32 °C (Davey et al., 1989; van Driel et al., 1994; Kestilä and Valkonen, 1994). In Figure 4.10, the IV – III (onset temperature of 32 °C) and III – II (onset temperature of 84 °C) phase transitions were not observed. TG analysis on the Type A AN prills did not indicate any moisture content (see Section 4.6). The prills were thus dry, and the absence of the 32 °C transition was not surprising.

The IV – V transition, which has an onset temperature of -18 °C (van Driel et al., 1994), was not observed from the DSC data. Instead, two phase transitions were obtained at -34 °C (on cooling) and at -6 °C (on heating); these phase transitions may result from a hysteresis of the phase change at -18 °C. On the other hand, the phase transition at -34 °C may also be the result of a transformation of AN from phase IV to VI. Phase VI of AN was recently identified by Shehap (1999) using infrared spectroscopy. Shehap (1999) also found the existence of another phase (number VII) with a transition temperature of -50 °C. However, this phase VI–VII transition is not observed from the DSC results for AN prills.

The phase transitions of AN that are observed are closely dependent on the temperature, crystallization method, moisture content, purity and previous thermal history

(Davey et al., 1989; Kestilä and Valkonen, 1994; van Driel et al., 1994). The observed variation in the low temperature phase transition between AN prills and the literature value for AN crystal may be due to some impurity (Section 4.3) and unknown aspects of the previous thermal history of the AN prills studied.

4.7.1.2 Cold-treatment

Cold-treated prills were prepared to test if the disintegration is a result from either a low or high temperature phase change, or the combined effect of both. After standing in dry ice ($-78\text{ }^{\circ}\text{C}$) for only 5 hours, disintegration of the AN prills is observed. The cold-treated prills are similar to the temperature-cycled prills in Figure 4.9. The disintegration of AN prills may be due to: (i) a structural and volume change as a result of the low temperature phase transition; (ii) a thermal shock caused by the rapid restoration from about $-78\text{ }^{\circ}\text{C}$ to room temperature.

To further identify the cause of the disintegration, other cold-treated AN samples were prepared using DSC. In order to reduce the possible thermal shock, the prills were cooled to the desired temperature and restored to room temperature using a ramp rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Since the DSC results (Figure 4.10) show that the low temperature phase transition of AN occurs at about $-34\text{ }^{\circ}\text{C}$, AN prills were kept isothermally at $-35\text{ }^{\circ}\text{C}$ for 5 hours. The DSC cold-treated prills show a similar disintegration as the temperature-cycled and the samples treated with dry ice (Figure 4.9).

The results imply that the prill fracture is unlikely to be caused by the thermal shock during the sample preparation. Apparently, the disintegration is caused by a drastic change in crystal lattice of the low temperature phase transition at $-34\text{ }^{\circ}\text{C}$. However, there

are no published crystal lattice data for AN phase VI, since it has only been identified recently (Shehap, 1999).

In practice, no disintegration of AN prills is observed under normal Canadian winter conditions, so that this low temperature phase transition may not be a practical problem in Canada. However, it may still result in unwanted prill fracture when the winter conditions result in temperatures lower than -35°C .

Although no IV – V phase transition was observed from the DSC results (Figure 4.10), AN prills may still be transformed to phase V when stored around -18°C for an extended period (just a normal winter climate in Canada). Such a transformation may cause a structure change and affect the wettability of AN prills. Therefore, the capillary penetration measurements were conducted on AN prills which had been placed in a domestic freezer ($\sim -22^{\circ}\text{C}$) for over 3 weeks. No disintegration was observed from this sample. There is also no difference in wetting rate of this sample compared with the as-received prills. The results imply that the IV – V phase transition still does not occur in AN prills kept at temperature of -22°C for extended periods. While it is possible that the transition does occur, it does not alter the wettability of AN prills.

4.7.1.3 Heat-treatment

As presented in Section 1.2.1, it is commonly known that in practice, repeated cycling between phase III and IV leads to disintegration of the AN. However, in this study, no disintegration was observed from the heat-treated prills.

A possible explanation is that the as-received AN prills are quite dry (see Section 4.6.1), and that the IV – III transition at 32°C does not occur (see Section 4.7.1.1).

Instead, the AN prills are transformed to phase II at 50 °C. On the other hand, the IV – III transition has a higher tendency to occur in practice, since AN prills may be exposed to humid air in summer.

Experiments were carried out to verify qualitatively the effect of moisture content on the disintegration of AN prills. A moisturized AN sample, which contained about 1 % moisture after exposure to moist air for 5 hours (see Section 4.6.1), was heated at 35 °C for 4 hours. After the heat-treatment, the moisturized AN prills did visually show some extent of disintegration, but not as significantly as the cold-treated sample and temperature-cycled samples in Figure 4.9. More severe disintegration may be produced with repeated heat-treatment. No wetting rates experiments were carried out in order to attempt to quantify this tendency.

4.7.2 Enhanced Wettability of Heat-treated AN Prills

As seen in Table 4.8, the capillary penetration results show that the wetting rate of the heat-treated prills is 70 % higher than the as-received prills. These heated-treated samples were prepared by placing as-received AN prills in the oven at 60 °C for 12

Table 4.8. Wetting rate of as-received and treated AN prills

Sample	10^3 Wetting rate/g ² min ⁻¹
As-received	2.68 ± 0.05
Desiccated	2.70 ± 0.02
Heat-treated at 60 °C	4.49 ± 0.28

hours. There are two possible reasons for the enhanced wettability: (i) a lower moisture content, and (ii) a morphology change in heat-treated prills.

If the substantial difference in wettability between the as-received and the heat-treated prills is primarily due to the moisture content, their difference in moisture content will be 2.65 mass %. This value was estimated by extrapolating the linear relationship between the wettability and the moisture content in Figure 4.7. In fact, the TG results have shown that there is no water on the surface and in the pores of the as-received prills (see Section 4.6.1).

Additionally, as seen in Table 4.8, there is no significant increase in the wetting rate of a desiccated sample prepared by placing it in the desiccator under vacuum for 14 days. However, the influence of moisture content cannot be completely ruled out, as the monolayer of water on AN surface may not desorb in TG ($< 110\text{ }^{\circ}\text{C}$), and also not under vacuum and desiccator conditions. However, the monolayer of water on the AN is unlikely to account for the substantial difference in the wetting rate between the as-received and the heat-treated prills.

On the other hand, the increased wettability may result from a morphology change of the AN prills during the IV – II phase transition. In a preliminary study of this transformation, wetting rate data were obtained from various samples which had been heated in an oven at 45 and 60 $^{\circ}\text{C}$ for various time intervals. The results suggest that this morphology change is temperature dependent, and the transformation could be complete within 30 min (Appendix I).

4.7.2.1 Kinetics of Phase Transformation

In order to study the kinetics of the IV – II phase transformation, various samples in a range of temperatures were prepared by heating the prills in vials in a hot-water bath for 4 hours. Note that generally a higher extent of transformation was obtained in the water bath than in the oven, i.e. higher wetting rates were obtained from samples heated in the water bath than in the oven at the same temperature, since the thermal conductivity of water is higher than that of air.

As shown in Figure 4.11, the wettability of the treated prills increases as the treatment temperature is raised. The wetting rate increases significantly at 45 °C, and begins to plateau starting at 55 °C. The results suggest that the transformation has an onset temperature between 40 and 45 °C, and is complete at 55 °C (at 4 hours). This phase transformation between 45 and 55 °C agrees with what was observed from DSC

Figure 4.11. Temperature effect on the wettability of AN prills. The error bars show standard deviation of 2 replicates.

(see Section 4.7.1.1), and thereby corresponds to the reported IV–II phase transition in the literature (see Section 1.2.1).

The kinetics of the IV – II phase transformation in AN prills were further investigated at three different temperatures. Temperatures of 45, 50 and 55 °C were selected according to the results in Figure 4.11. At temperature higher than 55 °C, the transition was found to be so fast that it was completed at 5 min. AN prills (contained in glass vials) were placed in the water bath, which had been set at the appropriate temperature. The samples were then removed from the test conditions at the various time points and quenched. The wetting rates (w) of these samples were then analyzed using capillary penetration measurements.

The fractional transformation (α) of AN prills was evaluated from the equation

$$\alpha = \frac{w - w_i}{w_f - w_i} \quad (4.1)$$

where w_i and w_f are the wetting rates of the sample in its initial and final state, respectively. The wetting rate of the as-received prills was used as the w_i . For the w_f , the wetting rate used is obtained from the sample heat-treated at 65 °C for 4 hours, which appears to correspond with complete transformation (Figure 4.11).

The α vs. time curves for the phase transformation at each of the temperature studied are shown in Figure 4.12. The curves are sigmoidal in shape, which is typical for solid-state transformation in bulk powder samples. Both the maximum extent of the transformation and the rate of transformation increase with an increase in temperature.

Figure 4.12. α vs. time curves for the phase transformation in AN prills

The phase transition was characterized using the Avrami-Erofeyev equation, which is widely used to describe the kinetics of solid-state phase transformations (Avrami, 1941; Erofeyev, 1946). The general relationship takes the form:

$$\alpha = 1 - \exp[-(kt)^n] \quad (4.2)$$

where k is the rate constant, and n can be: $3 \leq n \leq 4$ for three-dimensional growth, $2 \leq n \leq 3$ for two-dimensional growth, and $1 \leq n \leq 2$ for one-dimensional growth.

The Avrami-Erofeyev relationship assumes that the transformation proceeds by a nucleation-and-growth mechanism and takes into account the coalescence and ingestion of other nuclei as the new phase grows. Nucleation is assumed to be random, that is, if the entire sample were divided into small equal volumes, then the probability of a nucleus

forming in each element in unit time is the same. The theory also assumes isotropic growth (equivalent growth rate in all three crystallographic directions) and that the number of potential nucleation sites are limited.

The α vs. time data were analyzed using the Avrami-Erofeyev equation, and the value of n was determined from a plot of $\ln[-\ln(1 - \alpha)]$ vs. $\ln t$; an example of the plot is shown in Figure 4.13. The exponent n is given by the gradient of the plot, and a mean value for n of 2.6 ± 0.4 was obtained from the various isothermal temperatures. Such a value of n indicates two-dimensional growth.

The rate constants (k) were then estimated from plots of $-\ln(1 - \alpha)^{1/2.6}$ vs. time. An example of the plot is shown in Figure 4.14. The k values were estimated from the slope of a linear regression of the plots. As expected, the rate constant of the phase transformation increases as the temperature is raised, as shown in Figure 4.15 where the $\ln k$ is plotted against $1/T$.

Figure 4.13. Determination of the Avrami-Erofeyev exponent n at 55 °C

Figure 4.14. Avrami-Erofeyev plot for the phase transformation at 55 °C

Figure 4.15. Arrhenius plot for the phase transformation in AN prills

The empirical kinetic parameters were estimated from the plot of $\ln k$ vs. $1/T$ in Figure 4.15 using the Arrhenius equation:

$$k = Z \exp\left(-\frac{E_a}{RT}\right) \quad (4.3)$$

where Z is the pre-exponential factor, E_a is the activation energy and R is the gas constant. Values of $E_a = 36 \pm 4 \text{ kJ mol}^{-1}$ and $\ln(Z/\text{min}^{-1}) = 11 \pm 1$ are obtained from the slope and the intercept of a linear regression of the plot in Figure 4.15. The uncertainty of the values represents one standard deviation in the regression.

The magnitude of the activation energy for molecular crystals is within $100 - 200 \text{ kJ mol}^{-1}$ (Brown et al., 1980), and the pre-exponential factor in a solid-state transformation is commonly reconciled with the lattice vibration frequency which is of the order of 10^{13} s^{-1} , i.e. $\ln(Z/\text{min}^{-1}) = 34$. In this study, the values estimated for the activation energy and pre-exponential factor differ markedly from these expected ranges. The results indicate complications in the AN phase transformation; it should be noted that AN is an ionic rather than a molecular crystal. However, no literature values can be found for comparison of the kinetic parameters.

The sigmoidal α vs. time curve is typical of many solid-state phase transformations regardless of the underlying topological mechanism. Consequently, it can be difficult to distinguish between the various kinetic models purely on the basis of modelling the α vs. time data. This problem is compounded in this study when trying to analyze curves based on relatively few data points and where each determination may be imprecise. In this kinetic study, no replicate sample was prepared and analyzed; however, a respectable precision of the capillary penetration measurements has been demonstrated by the wetting rate data obtained for all the other samples in this investigation.

On the other hand, in this kinetic study, the sample is removed from its test conditions at the various time points, quenched, and then analyzed. This procedure can introduce error into the data since a change in the extent of transformation may occur during quenching and/or analysis. Ideally, data collection should be in situ and in real time, enabling the dynamic processes to be followed as they occur with the inherent accuracy, e.g. X-ray diffraction and DSC measurements. The kinetic study of the phase transformation in AN prills using the capillary penetration measurements is certainly not comparable to the accuracy obtained from other possible techniques.

However, the capillary penetration method is a simple technique which requires no special equipment and expensive reagents. These advantages may make this technique an economic alternative for kinetic analysis of solid-solid phase transformation, if the wetting rate of the sample changes after the phase transformation. Additionally, the results of this kinetic study demonstrate the sensitivity and reliability of the capillary penetration measurements for the determination of wetting rate.

4.8 Summary

From the comparison of the various AN prills, the wettability depends on the characteristics of the solid samples. The physical properties of AN prills that influence the measured wetting rate are porosity, adsorption capacity, bulk density, particle size and size distribution. The explosive-grade AN prills (Types A–C) show a better wettability due to a combined effect of these properties.

The wetting rate of AN powder is about 500 times that of normal prills. Finer powders have substantial higher wettability than AN in prills form. However, they also have higher tendencies to absorb moisture and to cake, which prevent the adsorption of fuel oil. The reduction in size must be carried out immediately before wetting if a higher wetting rate is to be consistently obtained.

The effects of moisture content and temperature on the wettability of AN prills were studied. The capillary penetration results show that the wettability of AN prills decreases linearly with increasing moisture content. For the effect of temperature, disintegration was observed from prills cycled through IV – VI and IV – III phase transitions.

On the other hand, prills passed through IV – II phase transition have wetting rates of 2.5 times that of as-received prills. The enhanced wettability may be due to a morphology change in the prills. Values of $E_a = 36 \pm 4 \text{ kJ mol}^{-1}$ and $\ln(Z/\text{min}^{-1}) = 11 \pm 1$ are obtained for this phase transformation from a kinetic study by means of the change in wetting rate data.

The accuracy of the kinetic study of the phase transformation in AN prills using the capillary penetration measurements is certainly not comparable to that obtained from other techniques. However, the results in this kinetic study demonstrate the sensitivity and reliability of the capillary penetration measurements for wetting rate determination.

CHAPTER 5: CONCLUSIONS

5.1 Feasibility of Various Experimental Methods Applied to AN Prills

The capillary penetration technique involves application of the Washburn equation to experimentally determine the rate of penetration of a liquid into a particle bed. The main deficiency of the model on which the Washburn equation is based is that only a single cylindrical capillary is used to characterize a complex porous network. Hence, the method cannot properly model the exact pathway of the liquid penetration in AN prills. However, the wetting rate data can be used as an empirical measure to compare the relative wettability of various AN prills. The sensitivity and simplicity of the capillary penetration technique makes it useful for comparing the wettability of samples.

The sessile drop technique is a simple and economical approach for determining the contact angles of liquids on the compacted surface of AN particles. However, it is questionable whether such contact angle measurements are representative of the wettability of AN prills, due to the microroughness, different surface composition and deformation of the compacted AN surface.

Scanning electron microscopy (SEM) was used to obtain a two dimensional view of pores of AN prills. The SEM observations had to be conducted at low accelerating voltage, because AN is extremely sensitive to the electron beam, and disintegrates at high accelerating voltage. SEM is only able to sample surface pores and a small fraction of the area of the sample. Although SEM is insufficient for evaluating the porosity of the entire

sample, it is a very important tool since it gives valuable insight into the pore structure of the area sampled.

X-ray microanalysis was used to chemically analyze the surface of AN samples, and various impurities were detected. However, the results may not be representative of the complete sample, since the surface was analyzed by a small spot X-ray microanalysis on a selected area of AN samples which have a non-uniform surface composition.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to analysis the moisture content and the phase transitions, respectively. Both techniques provide quick and reliable information about the AN samples.

5.2 Factors Affecting the Wettability of AN

The wettability of various AN prills with alkanes and fuel oil were compared. Factors influencing the wettability of AN prills include: surface tension, viscosity, density, purity, polarity and/or polarizability of the wetting liquid, as well as surface composition, porosity, bulk density, particle size, moisture content and thermal history of AN samples. Powders have significantly higher wettability than AN in prill form; however, they are also difficult to handle. The explosive-grade (porous) AN prills show a better wettability due to combined effects of the above factors.

The wetting rate of AN powders (with particle size of 125 – 250 μm) is about a factor 500 greater than of AN prills. The substantially higher wettability results from an increase in the total surface area and provision of a fresh clean surface for adsorption. However, powders also have a higher tendencies to absorb moisture and to cake, which

can prevent the adsorption of fuel oil. The reduction in size must be carried out immediately before wetting if a higher wetting rate is to be consistently obtained.

5.3 Suggestions for Future Work

There are several other aspects in this research project that would be of interest for further investigation:

- (i) The results from both sessile drop and capillary penetration measurements show that AN has a higher wettability with fuel oil, compared to that with alkanes. On the other hand, problems in terms of irreproducible and non-uniform wetting are also encountered. Hence, studies on the various components of fuel oil are required to more completely understand the enhanced wettability by fuel oil. Studies on the mixture of alkanes and aromatics in various proportions may also be used to investigate the effect of aromatics on the wettability of AN with mixtures. The study may also proceed with other types of liquids to understand the interactions of AN with liquids.
- (ii) Surfactants are frequently used to enhance wetting of the particle surface. In this study, the results of sessile drop and capillary penetration measurements on a mixture of heptane and a surfactant (polyoxyethylene sorbitan, approximately 0.5 %) do not show an effect on the wettability of AN. Further studies could be carried out with various different types of surfactants in order to select a surfactant which would increase the wettability of AN.

- (iii) AN prills contain different coatings and additives (e.g. kaolinite, talc) to prevent the adsorption of moisture. To determine the effect of those coating or additives on the wetting of AN prills, comparison of AN prills with and without coating is required. However, AN is very hygroscopic without the coating. Hence, it would be difficult to eliminate the effect of moisture and to obtain valid results from capillary penetration measurement. Alternatively, wettability studies on those coatings and additives per se may provide hints on their effect on the wettability of AN. A quantitative analysis on the AN surface composition is also required to determine the extent of those effects.
- (iv) The size distribution of the prills can alter the bulk density and the void fraction, thereby affecting the wettability of AN prills. An investigation on the optimum ratio of size distribution of porous AN prills is suggested to maximize the wettability of AN prills.
- (v) The wetting rate of AN powder after temperature-cycling (with particle size of 125 – 250 μm) is about a factor of 500 greater than AN prills. However, powders also have a higher tendency to absorb moisture and to cake, which prevents the adsorption of fuel oil. A study of the effect of moisture on the caking tendency and wettability of uncoated AN powder may be of interest.
- (vi) SEM has been used to obtain a two dimensional view of pores in AN prills. However, it is insufficient for evaluating the percentage of pore structure. Further studies could be carried out with 3-D nuclear magnetic resonance microscopy or high-resolution thermogravimetry for estimating the porosity of various porous prills.

- (vii) Kinetic parameters of AN of the IV – II phase transformation were determined using the change in wetting rates. However, no literature values can be found for comparison. The results from capillary penetration may possibly be verified by kinetic studies using a more reliable method such as X-ray diffraction or differential scanning calorimetry.

CHAPTER 6: REFERENCES

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APPENDIX I

RESULTS OF CAPILLARY PENETRATION MEASUREMENTS

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Sample: Type A AN prills
Particle size: $1.68 < < 2.0$ mm
Liquid: heptane

Sample: Type A AN prills
Particle size: $1.68 < < 2.0$ mm
Liquid: octane

Sample: Type A AN prills
Particle size: $1.68 < < 2.0$
Liquid: nonane

Sample: Type A AN prills
Particle size: $1.68 < < 2.0$
Liquid: dodecane

Sample: Type A AN prills
Particle size: $1.68 < < 2.0$ mm
Liquid: hexadecane

Sample: Type A AN prills
Particle size: $1.68 < < 2.0$ mm
Liquid: dissel fuel

Summary of wetting rates for Type A AN prills (1.7 – 2.0 mm) with various liquids

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Heptane	13	22	46	0.820	2.75
	20	23	61	0.819	2.94
	56	25	30	0.820	2.80
				0.820 ± 0.006	2.83 ± 0.10
Octane	54	25	40	0.820	2.13
	55	25	38	0.820	1.84
					1.97 ± 0.18
Nonane	52	25	45	0.819	1.27
	53	25	42	0.819	1.21
					1.24 ± 0.04
Dodecane	42	25	47	0.820	0.75
	43	26	43	0.794	0.68
	49	25	45	0.820	0.68
					0.70 ± 0.04
Hexadecane	45	25	49	0.820	0.46
	46	26	47	0.820	0.41
	48	25	50	0.807	0.39
					0.42 ± 0.04
Heptane + polyoxyethylene sorbitan (~ 0.5 %)	33	23	36	0.820	2.72
	38	25	43	0.820	2.90
					2.81 ± 0.13
Diesel fuel	123	23	< 20	0.834	0.93
	124	24	< 20	0.833	1.40
					1.16 ± 0.33

Summary of wetting rates for various AN prills with heptane

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Type A	39	25	57	0.820	2.75
	40	26	55	0.820	2.68
	41	26	49	0.834	2.64
	85	23	21	0.833	2.67
				0.827 ± 0.008	2.68 ± 0.05
Type B	22	25	54	0.746	2.51
	24	21	43	0.757	2.49
	26	20	56	0.758	2.18
				0.754 ± 0.007	2.39 ± 0.18
Type C	27	21	51	0.769	2.18
	29	22	43	0.746	2.09
	31	23	39	0.757	2.51
				0.757 ± 0.011	2.26 ± 0.22
Type D	23	20	43	0.961	1.35
	25	22	42	0.980	1.20
	28	21	46	0.980	1.05
				0.974 ± 0.011	1.20 ± 0.15
Type E	60	23	23	0.910	0.66
	62	25	42	0.918	0.68
				0.914 ± 0.006	0.67 ± 0.02

Summary of wetting rates for Type A AN prills in different sizes with heptane

Size/mm	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
1.0 < < 1.4	6	23	55	0.862	2.18
	8	23	69	0.862	2.11
	17	24	61	0.877	2.46
	19	23	53	0.862	2.15
				0.866 ± 0.007	2.22 ± 0.16
1.4 < < 1.68	11	21	54	0.847	2.62
	14	22	69	0.833	2.66
	16	24	66	0.820	2.39
	21	25	55	0.848	2.94
				0.837 ± 0.013	2.65 ± 0.22
1.68 < < 2.0	13	22	46	0.820	2.75
	20	23	61	0.819	2.94
	56	25	30	0.820	2.80
				0.822 ± 0.006	2.65 ± 0.26
2.0 <	10	23	55	0.769	2.45
	12	22	49	0.781	2.52
	15	23	69	0.794	2.76
	18	25	59	0.781	2.71
				0.781 ± 0.010	2.61 ± 0.15

Summary of wetting rates for AN powders with hexadecane

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Ground powder	70	25	29	1.000	70.00
	73	27	25	0.975	81.00
				0.987 ± 0.018	75 ± 8
TC powder	71	25	29	0.781	196.00
	72	26	26	0.726	232.00
				0.753 ± 0.039	214 ± 18

Summary of wetting rates for moisturized AN prills

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Wetted 1.5 h (0.46 % water)	83	22	22	0.788	2.57
	84	22	21	0.800	2.62
				0.794 ± 0.008	2.59 ± 0.03
Wetted 5 h (1.10 % water)	100	26	35	0.811	1.83
	109	24	27	0.817	1.99
				0.814 ± 0.004	1.91 ± 0.11
Wetted 3 h (2.18 % water)	76	26	36	0.820	1.22
	80	28	43	0.820	1.25
				0.820 ± 0.000	1.23 ± 0.02
Wetted 6 h (2.42 % water)	75	28	35	0.826	1.16
	81	24	40	0.820	1.25
				0.823 ± 0.004	1.20 ± 0.06
Wetted 12 h (3.79 % water)	77	26	32	0.848	0.34
	86	25	53	0.926	0.25
				0.89 ± 0.05	0.29 ± 0.06

Summary of wetting rates for treated Type A AN prills

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Desciated Rm T (vacuum)	57	23	24	0.833	2.72
	58	23	22	0.833	2.69
				0.833 ± 0.000	2.70 ± 0.02
Heat-treated 45 °C	68	23	27	0.820	3.36
	69	23	26	0.820	3.25
				0.820 ± 0.000	3.30 ± 0.08
Heat-treated 60 °C (exposed)	30	22	42	0.793	4.29
	32	23	37	0.757	4.69
	59	23	24	0.833	4.49
				0.775 ± 0.025	4.49 ± 0.28
Wetted normal (4 h)	63	24	45	0.807	1.15
	66	25	38	0.794	1.38
				0.800 ± 0.009	1.26 ± 0.16
Wetted H-treated (4 h)	64	24	45	0.820	1.93
	65	24	35	0.794	1.72
				0.807 ± 0.018	1.82 ± 0.15
Wetted normal (6 h)	75	28	35	0.826	1.16
	81	24	40	0.820	1.25
				0.823 ± 0.004	1.20 ± 0.06
Wetted H-treated (6 h)	74	28	35	0.813	1.02
	82	24	40	0.813	1.08
				0.813 ± 0.000	1.05 ± 0.04

Summary of wetting rates for heat-treated Type B AN prills

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Heat-treated 60 °C	34	23	36	0.735	4.96
	37	25	42	0.735	5.07
				0.735 ± 0.000	5.01 ± 0.08

Summary of wetting rates for heat-treated Type D AN prills

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
Heat-treated 60 °C	35	23	35	0.981	2.07
	36	24	40	0.962	1.91
				0.971 ± 0.013	1.99 ± 0.11

Summary of wetting rates for heat-treated Type A AN prills (oven at 60 °C)

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
HT 5 min	90	24	30	0.833	3.39
HT 30 min	91	25	32	0.826	4.15
HT 60 min	92	26	32	0.813	4.48
HT 1 day	87	24	34	0.840	4.84
HT 3 days	88	24	31	0.813	5.05

Summary of wetting rates for heat-treated prills (water bath)

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
T = 35 °C	93	24	27	0.847	3.32
T = 40 °C	104	25	30	0.855	3.45
T = 45 °C	96	26	35	0.820	5.54
T = 50 °C	102	25	26	0.833	6.26
T = 55 °C	105	25	30	0.833	6.68
T = 60 °C	107	24	30	0.833	6.69
T = 65 °C	95	25	35	0.826	6.78

Summary of wetting rates for heat-treated prills at 45 °C

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
10 min	118	24	< 20	0.833	2.90
12.5 min	117	24	< 20	0.847	3.08
15 min	116	23	< 20	0.841	3.73
240 min	96	26	35	0.820	5.54

Summary of wetting rates for heat-treated prills at 50 °C

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
5 min	115	23	< 20	0.826	2.97
10 min	114	24	< 20	0.826	3.82
15 min	113	24	< 20	0.833	5.78
45 min	111	23	< 20	0.826	6.29
240 min	102	25	26	0.833	6.26

Summary of wetting rates for heat-treated prills at 55 °C

Sample	Data file	T/°C	Humidity %	Bulk density /g cm ⁻³	10 ³ Slope /g ² min ⁻¹
5 min	122	24	< 20	0.820	3.30
10 min	121	24	< 20	0.827	4.94
13 min	120	23	< 20	0.820	5.72
15 min	119	23	< 20	0.833	6.38
240 min	105	25	30	0.833	6.68

APPENDIX II

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Type A AN prills (external) **Type A AN prills (internal)** **Type B AN prills (external)** **Type B AN prills (internal)**

Type C AN prills (external) **Type C AN prills (internal)** **Type D AN prills (external)** **Type D AN prills (internal)**

Type E AN prills (external) **Type E AN prills (internal)** **Moisturized Type A AN prills**

Temperature-cycled Type A AN prills **Cold-treated Type A AN prills (dry ice)** **Heat-treated Type A AN prills (oven at 45 °C)**

Heat-treated Type A AN prills (oven at 60 °C) **Ground powders** **Broken T-cycled prills** **AN reagent** **AN pellets (compacted prills)** **AN pellets (compacted reagent)**

APPENDIX III:

X-RAY MICROANALYSIS RESULTS

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Type A AN prills

External surface

External surface

External surface

Internal surface

Type B AN prills

External surface

External surface

External surface

Internal surface

Type C AN prills

External surface

External surface

External surface

Internal surface

Type D AN prills

External surface

External surface

External surface

Internal surface

Type E AN prills

External surface

External surface

External surface

Internal surface

Powder ground from Type A AN prills

AN pellets

Compacted reagent

Compacted reagent

Compacted prills

Compacted prills

AN reagents

APPENDIX IV

TG RESULTS FOR MOISTURE ANALYSIS

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As-received Type A AN prills	119
Moisturized AN prills - 1.5 h	121
Moisturized AN prills - 3.0 h	122
Moisturized AN prills - 5.0 h	123
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Sample: AN Pills
Size: 17.7980 mg
Method: Ramp 5 °C/min to 250°C
Comment: 100mL/min N2 (60/40)

TGA

File: C:\TA\Data\TGA\An.358
Operator: Q. Kwok
Run Date: 9-Jan-01 08:03

Sample: AN Pills
Size: 13.0680 mg
Method: Ramp 5 °C/min to 200°C

TGA

File: C:\TA\Data\TGA\An.352
Operator: Q. Kwok
Run Date: 2-Jan-01 10:29

Sample: Wetted AN Pills (1.5 hr)
Size: 27.3180 mg
Method: Ramp 5 °C/min to 120 °C

TGA

File: C:\TA\Data\TGA\An.312
Operator: Q. Kwok
Run Date: 24-Oct-00 14:51

Sample: Wetted AN Pills (1.5 hr)
Size: 33.0570 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TA\Data\TGA\An.318
Operator: Q. Kwok
Run Date: 25-Oct-00 07:41

Sample: Wetted AN Pills (3.0 hr)
Size: 30.8910 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TA\Data\TGA\An.313
Operator: Q. Kwok
Run Date: 24-Oct-00 15:26

Sample: Wetted AN Pills (3 hr)
Size: 36.3660 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TA\Data\TGA\An.319
Operator: Q. Kwok
Run Date: 25-Oct-00 08:18

Sample: Wetted AN Pills
Size: 32.0430 mg
Method: Ramp
Comment: Ramp 5 °C/min to 110 °C

TGA

File: C:\TA\Data\TGA\An.340
Operator: Q. Kwok
Run Date: 8-Nov-00 15:26

Sample: Wetted AN Pills
Size: 26.4210 mg
Method: Ramp
Comment: Ramp 5 °C/min to 110 °C

TGA

File: C:\TA\Data\TGA\An.341
Operator: Q. Kwok
Run Date: 8-Nov-00 16:07

Sample: Wetted AN Pills (6 hr)
Size: 40.6850 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TAI\Data\TGA\An.324
Operator: Q. Kiwok
Run Date: 25-Oct-00 11:44

Sample: Wetted AN Pills (6 hr)
Size: 35.6770 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TAI\Data\TGA\An.326
Operator: Q. Kiwok
Run Date: 25-Oct-00 14:39

Sample: Wetted AN Pills (12 hr)
Size: 28.5580 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TAIData\TGA\An.317
Operator: Q. Kwok
Run Date: 24-Oct-00 17:18

Sample: Wetted AN Pills (12 hr)
Size: 32.0330 mg
Method: Ramp 5 °C/min to 110 °C

TGA

File: C:\TAIData\TGA\An.323
Operator: Q. Kwok
Run Date: 25-Oct-00 11:11

APPENDIX V

DSC RESULTS FOR ANALYSIS OF PHASE TRANSITIONS

Sample: AN Prill A
Size: 12.5790 mg
Method: Ramp 140 to -75 to 150
Comment: Cell 6 MCA; 5°C/min -75 to 150°C; 50 mL/min N2

DSC

File: C:\TA\Data\DSC\An.442
Operator: Queenie Kwok
Run Date: 27-Feb-01 09:50

Sample: AN Prill A
Size: 18.7040 mg
Method: Ramp 140 to -75 to 150
Comment: Cell 6 MCA; 5°C/min -75 to 150°C; 50 mL/min N2

DSC

File: C:\TA\Data\DSC\An.443
Operator: Queenie Kwok
Run Date: 27-Feb-01 13:16

APPENDIX VI

GC-MS RESULTS FOR FUEL OIL

Chromatogram Plot

File: E:\F02

Date: Mar-22-2001 14:55:01

Comment: DIESEL FUEL

Scan No: 2820

Retention Time: 47:00

RIC: 78232

Mass Range: 55 - 429

Plotted: 1 to 2820

Range: 1 to 2820

100% = 4516003

1	perdeuterobenzene C_6D_6	8	pentyl-cyclohexane $C_{11}H_{22}$
2	trimethylbenzene C_9H_{12}	9	undecane $C_{11}H_{24}$
3	octane C_8H_{18}	10	dodecane $C_{12}H_{26}$
4	nonane C_9H_{20}	11	tridecane $C_{13}H_{28}$
5	2-methyldecane $C_{11}H_{24}$	12	tetradecane $C_{14}H_{30}$
	+ 2-methylnaphthalene $C_{11}H_{10}$	13	pentadecane $C_{15}H_{32}$
6	decane $C_{10}H_{22}$	14	hexadecane $C_{16}H_{34}$
7	dimethylnaphthalene $C_{12}H_{12}$		