The Potential of Nanoparticle Enhanced Ionic Liquids (NEILs) as Advanced Heat Transfer Fluids

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INTRODUCTION

Interest in capturing the energy of the sun is rising as demands for renewable energy sources increase. One area of developing research is the use of concentrating solar power (CSP), where the solar energy is concentrated by using mirrors to direct the sunlight towards a collector filled with a heat transfer fluid (HTF).[1] The HTF transfers the collected energy into pressurized steam, which is used to generate energy. The greater the energy collected by the HTF, the more efficent the electrical energy production is, thus the overall efficiency is controlled by the thermal fluid. Commercial HTFs such as Therminol® (VP-1), which is a blend of biphenyl and diphenyl oxide,[2] have a significant vapor pressure, especially at elevated temperatures.[1] In order for these volatile compounds to be used in CSP systems, the system either has to be engineered to prevent the phase change (i.e., volatilization and condensation) through pressurization of the system, or operate across the phase change.[3]

Over thirty years ago, a class of low-melting organic compounds were developed with negligible vapor pressure.[4] These compounds are referred to as ionic liquids (ILs), which are organic-based compounds with discrete charges that cause a significant decrease in their vapor pressure.[5] As a class, ILs are molten salts with a melting point below $100\,^{\circ}C$ and can have a liquidus range approaching $400\,^{\circ}C$, and in several cases freezing points being below $0\,^{\circ}C$.[6] Due to the lack of an appreciable vapor

pressure, volatilization of an IL is not possible at atmospheric pressure,[5] which would lead to a simplification of the design if used as a thermal fluid and for energy storage materials.[7] Though the lack of a vapor pressure does not make the use of ILs a better HTF, the lack of a vapor pressure is a compliment to their higher heat capacity, higher volummetric density, and thus higher volumetric heat capacity.[8] These favorable physical properties give ILs a pontential advantage over the current commerically used thermal fluids. Also within the past decade nanofluids have gained attention for thermal conductivity enhancment of fluids[9], but little analysis has been completed on the heat capacity effects of the nanoparticle addition.

The idea of ILs or nanofluids as a HTF is not new, as there are several references that have proposed the idea.[8, 10] However, the use of ionic liquid nanofluids containing nanomaterials other than carbon nanotubes has never before been studied. Here, for the first time, nano-particle enhanced ILs (NEILs) have been shown to increase the heat capacity of the IL with no adverse side effects to the ILs' thermal stability and, only at high nanoparticle loading, are the IL physical properties affected. An increase of volumetric heat capacity translates into a better heat transfer fluid as more energy is stored per volumetric unit in the solar concentrating section, thus more efficency in increased steam pressure. Results show that the properties of the NEIL are highly dependant on the suspended nanomaterial and careful materials selection is required to fully optimize the nanofluid properties.

RESULTS AND DISCUSSION

Physical Properties

A good HTF needs to have the ability to absorbe a significant amount of energy in a given volume, as the geometry is dictated by the system design. Based on this, the volumetric heat capacity, which is a function of the heat capacity and the density, is a very important physical property to evaluate the NEILs against the traditional volatile organic thermal fluid, in this case VP-1®, and the neat ILs. 1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mmim][NTf_2]$) was selected as it is commerially avaliable from a wide range of vendors, has a tolerable viscosity, and good

thermal stability.[11]   The methyl blocking of the C-2 proton should decrease the chances of a catalytic/carbene-like interaction[12] with the nanoparticles with minimal effect on the viscosity. In Table 1, the heat capacity and density of [C_4mmim][NTf_2], and NEILs with 50 nm Al_2O_3 or 4 nm carbon black (CB) are compared at 80 and 200°C. Plots of the heat capacity curves from 60 to 360°C are available in the Supplemental Information. Nanoparticle loading of greater than 2.5 wt.% showed minimal increase in the heat capacity, and any gained benefit would be overshadowed by the adverse effects to the other IL physical properites, i.e., significant increase to the viscosity, as shown in Figure 1. The addition of the nanoparticles lead to an increase in the density of 10% for the Al_2O_3 NEILs, but a decrease of about 10% for the CB NEIL. A significant increase, about 40%, in the volumetric heat capacity was observed for the Al_2O_3 NEILs, but a decrease of about 30% for the CB NEILs. In this case, the increase volumetric heat capacity for the Al_2O_3 would make it a viable thermal fluid, but the CB NEILs exhibited a volumetric heat capacity lower than that for the neat IL and VP-1®. The decrease in heat capacity for the CB NEIL may be due to the increased thermal conductivity of the system, as carbonaceous materials are known to have very high thermal conductivity.[13] In nanocrystalline materials, a larger grain size will also correlate to a higher heat capacity.[14] VP-1® containing nanoparticles could not be tested in this study because of the high volatility of the fluid. We are currently devloping methods to measure heat capacity and thermal stability in a pressurized environment in order to characterize VP-1® containing nanoparticles for comparison to NEILs. Though this increased volumetric heat capacity for the Al_2O_3 NEIL is very important, the thermal stability can not be adversely effected if NEILs are going to be viable HTFs.

In addition to high heat capacity, good thermal conductivity and heat transfer coefficients for the fluids are needed. The neat IL [C_4mmim][Tf_2N] has a reported thermal conductivity of 0.125-0.12 W/m.K from 10-70°C [15], which is slightly lower than the 0.137- 0.131 W/m.K reported for VP-1® [2] over the same range and 20% of that of DI water. The thermal conductivity of base fluids has been reported to increase significantly with both Al_2O_3 and carbon based materials [16]. Our initial results suggest that 3% addition of nanoparticles will increase the thermal conductivity by 7% [17]. This increase

is a function of the wetting of the nanoparticle, where a greater interaction between the fluid and the nanoparticle will lead to a greater increase in the thermal conductivity of the nanofluid.

Thermal Stability

For the use of ILs or NEILs as a thermal fluid, long term thermal stability is even more important than the dynamic heating. In a concentrating solar power process, an IL or NEIL will be exposed to an elevated temperature for an extended amount of time as the fluid is heated and circulated through the closed loop to a secondary steam generating heat exchanger. Long term heating (i.e., 120 min at a static temperature before being heated to the next temperature) tests were performed as a means to evaluate the long term thermal stability under an inert environmnet, Table 2. The NEIL did not have an adverse effect on the thermal stability in a non-pressurized system and demonstrated a significant increase in the thermal stability under static heating compared to VP-1®.

Results from Table 2 should not be inferred as rates of decompostion of bulk material. The results presented here are used for internal comparision as all the parameters (e.g., surface area, mass, depth of IL, void headspace, etc.) are nominally equivalent. The decomposition rates do not become significant until temperatures above 300 ^{o}C. In an unpresserized system, this temperature is significantly higher than what is seen for VP-1® [2]. The effects of pressure are not yet known on the thermal stability of ILs and NEILs, and are currently being investigated.

CONCLUSIONS

Initial data supports the concept of NEILs as a viable heat transfer fulid for CSP systems. The ILs' high heat capacity and density yield a signficantly higher volumetric heat capacity compared to the commerically avaliable heat transfer fluids. These properties can be further improved by the addition of nanoparticles which yeild a new subclass of ILs, NEILs, though not all NEILs will lead to an enchancment of properties. The Al$_2$O$_3$ NEILs demonstrated a 30% increase in the heat capacity and paired with the increased density, a 40% increase in the volumetric heat capacities over neat IL and 70% over VP-1®. This increase in the heat capacities is complimented by little to no adverse effect on

the thermal stability of the IL. The ILs and NEILs demonstrated a significant improvemment in the thermal stability without volatization, and thus could provide an alternative to current volatile HTFs.

Supporting Information Available. Supporting Information includes: (1) experimental procedures, (2) viscosity of NEIL versus weight percent nanomaterial, (3) graphical depiction of effect of weight percent of nanomaterials on heat capacity (4) dynamic decomposition data

Table 1: Comparison of Density, Heat Capacity, and Volumetric Heat Capacity for VP-1, [C$_4$mmim][NTf$_2$] and NEILs.

	Density (g/mL)		Heat Capacity (J/g K)		Volumetric Heat Capacity (J/mL K)	
Temperature (^{o}C)	*80*	*200*	*80*	*200*	*80*	*200*
VP-1[2]	1.02	0.87	1.73	2.18	1.76	1.90
[C$_4$mmim][NTf$_2$]	1.37	1.29	1.53	1.84	2.10	2.37
IL w/ 0.5 $_{wt.}$% Al$_2$O$_3$	1.39	1.16	1.70	1.99	2.36	2.31
IL w/ 1.0 $_{wt.}$% Al$_2$O$_3$	1.43	1.20	1.93	2.35	2.75	2.82
IL w/ 2.5 $_{wt.}$% Al$_2$O$_3$	1.51	1.32	2.02	2.40	3.05	3.17
IL w/ 0.5 $_{wt.}$% CB	1.39	1.26	1.34	1.40	1.86	1.76
IL w/ 1.0 $_{wt.}$% CB	1.39	1.23	1.14	1.35	1.58	1.66
IL w/ 2.5 $_{wt.}$% CB	1.23	1.21	1.09	1.28	1.34	1.55

Table 2: Static decomposition rates of $[C_4mmim][NTf_2]$ and $[C_4mmim][NTf_2]$-based NEILs.

	Percent Mass Loss per Hour ($_{wt.}\%/h$)								
Temperature (^oC)	*200*	*225*	*250*	*275*	*300*	*325*	*350*	*375*	*400*
$[C_4mmim][NTf_2]$	<0.1	<0.1	<0.1	0.2	0.4	1.4	4.1	10.3	17.6
$[C_4mmim][NTf_2]$ 0.5 $_{wt/}\%$ Al_2O_3	<0.1	<0.1	<0.1	0.3	0.9	2.4	5.2	11.8	20.2
$[C_4mmim][NTf_2]$ 1.0 $_{wt/}\%$ Al_2O_3	<0.1	<0.1	<0.1	0.2	0.7	3.2	8.9	15.5	23.4
$[C_4mmim][NTf_2]$ 2.5 $_{wt/}\%$ Al_2O_3	<0.1	<0.1	<0.1	0.2	0.7	3.3	8.5	15.5	22.2
$[C_4mmim][NTf_2]$ 0.5 $_{wt/}\%$ CB	<0.1	<0.1	0.2	0.4	1.0	2.0	5.2	19.3	22.9
$[C_4mmim][NTf_2]$ 1.0 $_{wt/}\%$ CB	<0.1	<0.1	<0.1	0.2	0.8	2.5	6.0	13.1	19.1
$[C_4mmim][NTf_2]$ 2.5 $_{wt/}\%$ CB	<0.1	<0.1	0.1	0.5	1.0	3.0	6.0	13.1	22.5

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Supplemental Information for Energy & Fuels

The Potential of Nanoparticle Enhanced Ionic Liquids (NEILs) as Advanced Heat Transfer Fluids

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Experimental

To create the NEIL, two different types of nanoparticles were used, carbon black (Ketjen black, BASF) and Al_2O_3 spheres (Aldrich Chemical Co.). In all cases, the base ionic liquid was 1-butyl-2,3-dimethylimidazolium bis(triflouromethylsulfonyl)imide [C_4mmim][Tf_2N] obtained from IoLiTec. The ionic liquid was treated with activated charcoal, and filtered before use. All NEIL were made based on weight percentage. The weighed materials were added together in a glass vial and shaken with a vortex mixer for 15 minutes on a medium-high setting.

The physical properties of the nanomaterials were determined utilizing a Micromeritics ASAP 2020C, with a 17-point N_2 adsorption-desorption isotherms at 77K.

Viscosity was measured using the cone and plate method on a Thermo Haake MARS III with Rheowin software. A 0.5° titanium cone and flat plate was used. All measurements were conducted at 25°C and duplicated. The instrument was calibrated with the appropriate NIST standard for the viscosity window of the material.

Heat capacity was measured using a Netzsch DSC 404 with a silver furnace between 40-400°C. The values for heat capacity were determined using the ASTM defined methods.[1] All measurements were conducted at least five times to ensure accuracy and representative data is shown with a calculated error of 15% or less.

Results and Discussion

Table 1: Physical properties of nanomaterials used, determined by BET.

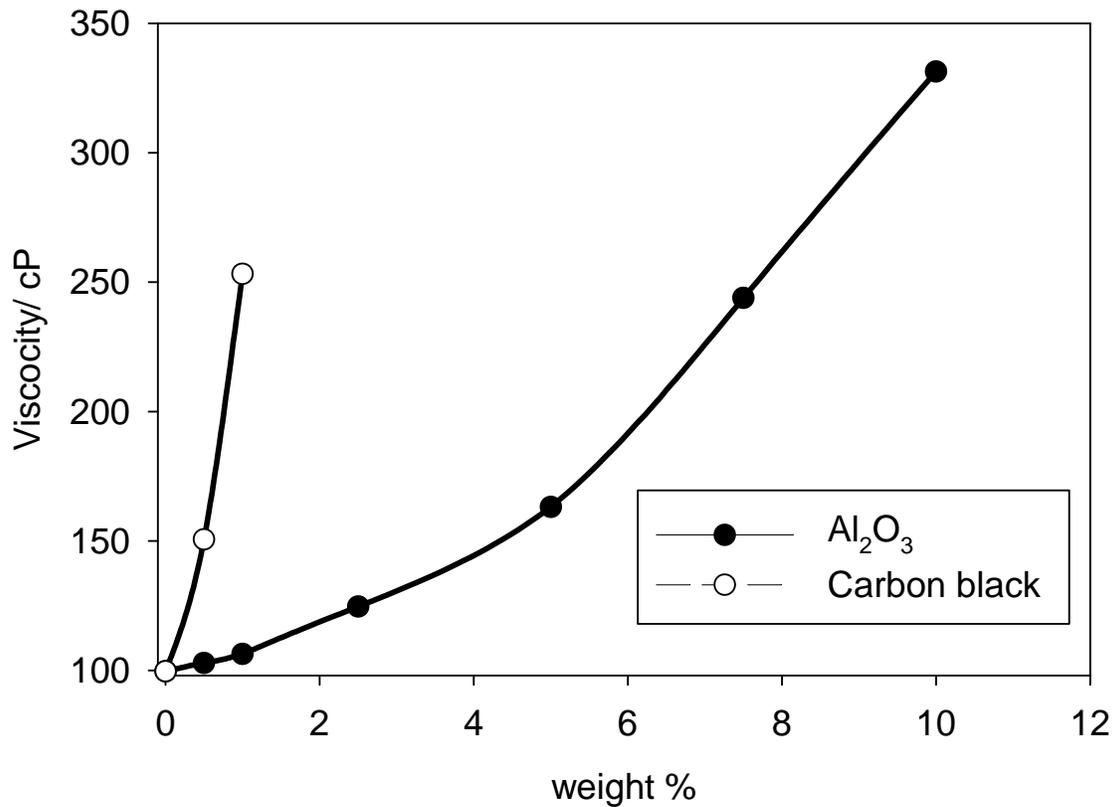|	Carbon black	Al_2O_3
Surface area/ m^2/g	1410.2	142.4
Pore size/ nm	7.7	22.3
Pore volume/ cm^3/g	2.7	0.8
Average particle size/ nm	4.3	42.1

Figure1: Viscosity versus weight percent of nanomaterial in [C$_4$mmim][NTF$_2$] at 25 ^{o}C

The viscosity of the NEILs with various weight percentages was measured at 25°C. The nanoparticles characteristics had a large influence on the viscosity of the resulting nanofluids. When carbon black was used, the viscosity increased 50% with the addition of only 0.5 wt% of material. At weight percents above 1%, the ionic liquid was completely absorbed by the carbon black; therefore, the viscosity was not measured. When Al$_2$O$_3$ was used, the viscosity changes were much more gradual. The viscosity increased by 6% with a 1 wt% addition, with much larger increases occurring at 2.5 wt% and above. The differences in behavior of the NEILs are attributed to the different physical properties of the nanomaterials, as seen in Table 1. The larger surface area and pore volume enabled better absorption of the IL in the carbon black, which drastically affected the viscosity. Further testing is underway to determine the effects based on the particle size of the material.
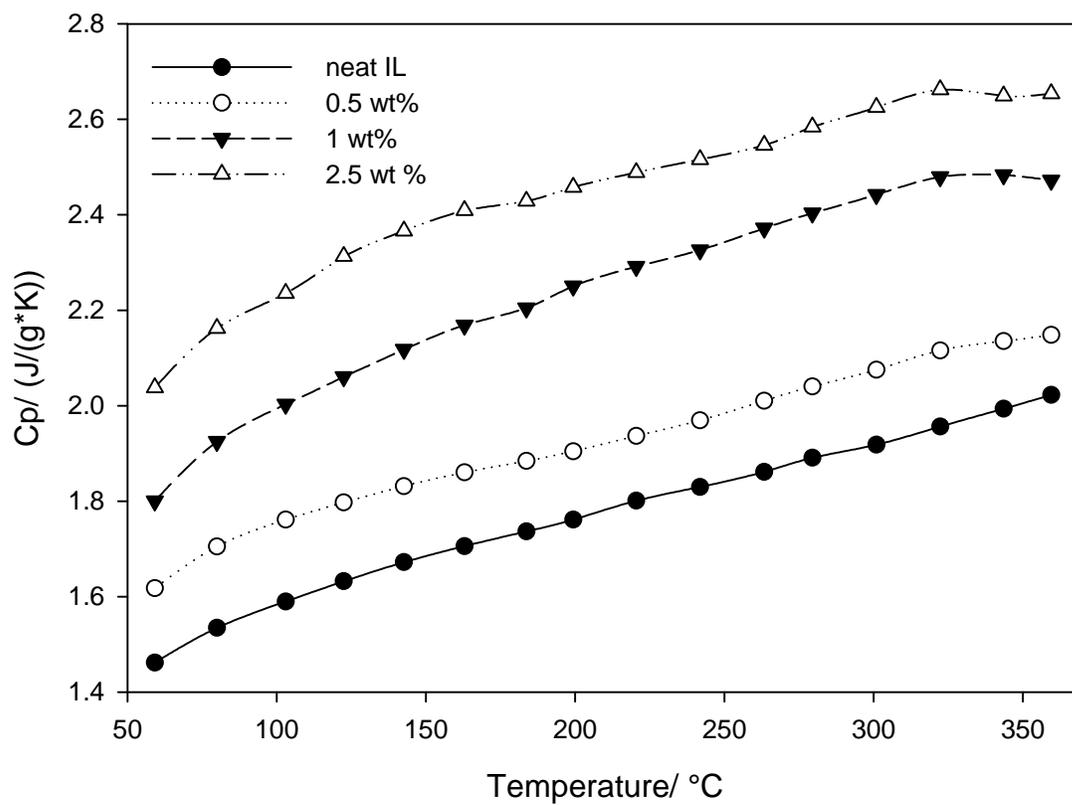
Figure 2: Heat Capacity versus temperature from 60 to 360°C for [C$_4$mmim][Tf$_2$N] and the NEIL with 0.5 – 2.5 weight percent of Al$_2$O$_3$.
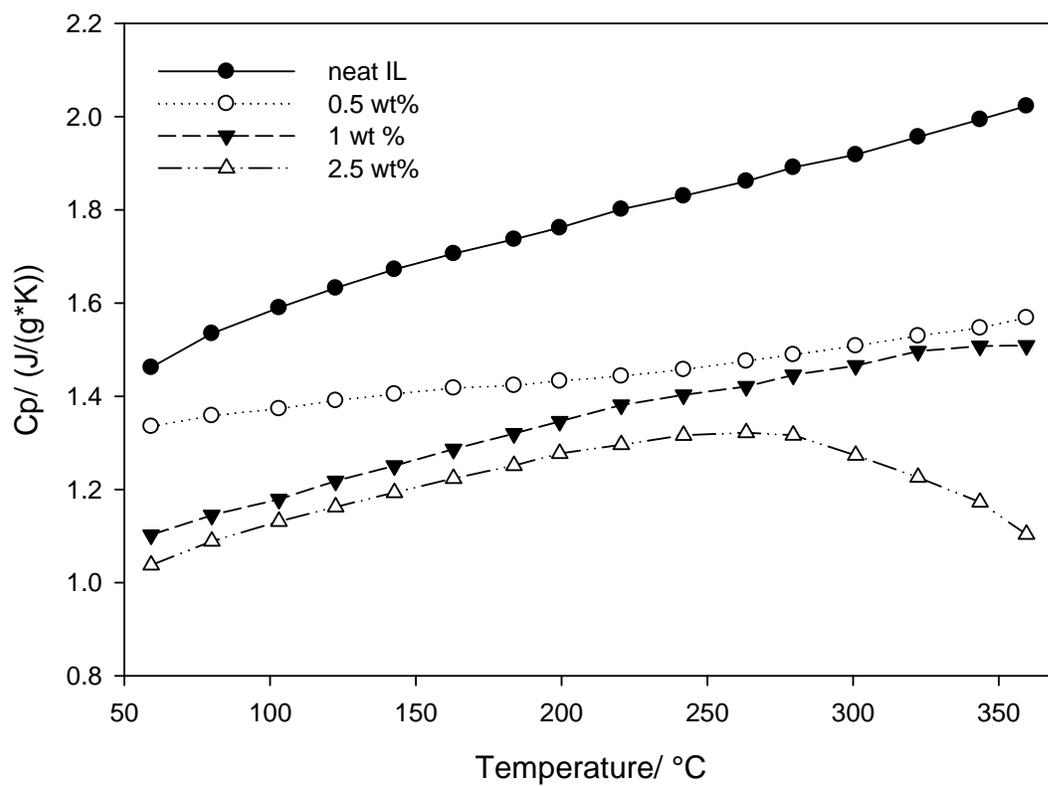
Figure 3: Heat Capacity versus temperature from 60 to 360°C for [C$_4$mmim][Tf$_2$N] and the NEIL with 0.5 – 2.5 weight percent of carbon black.
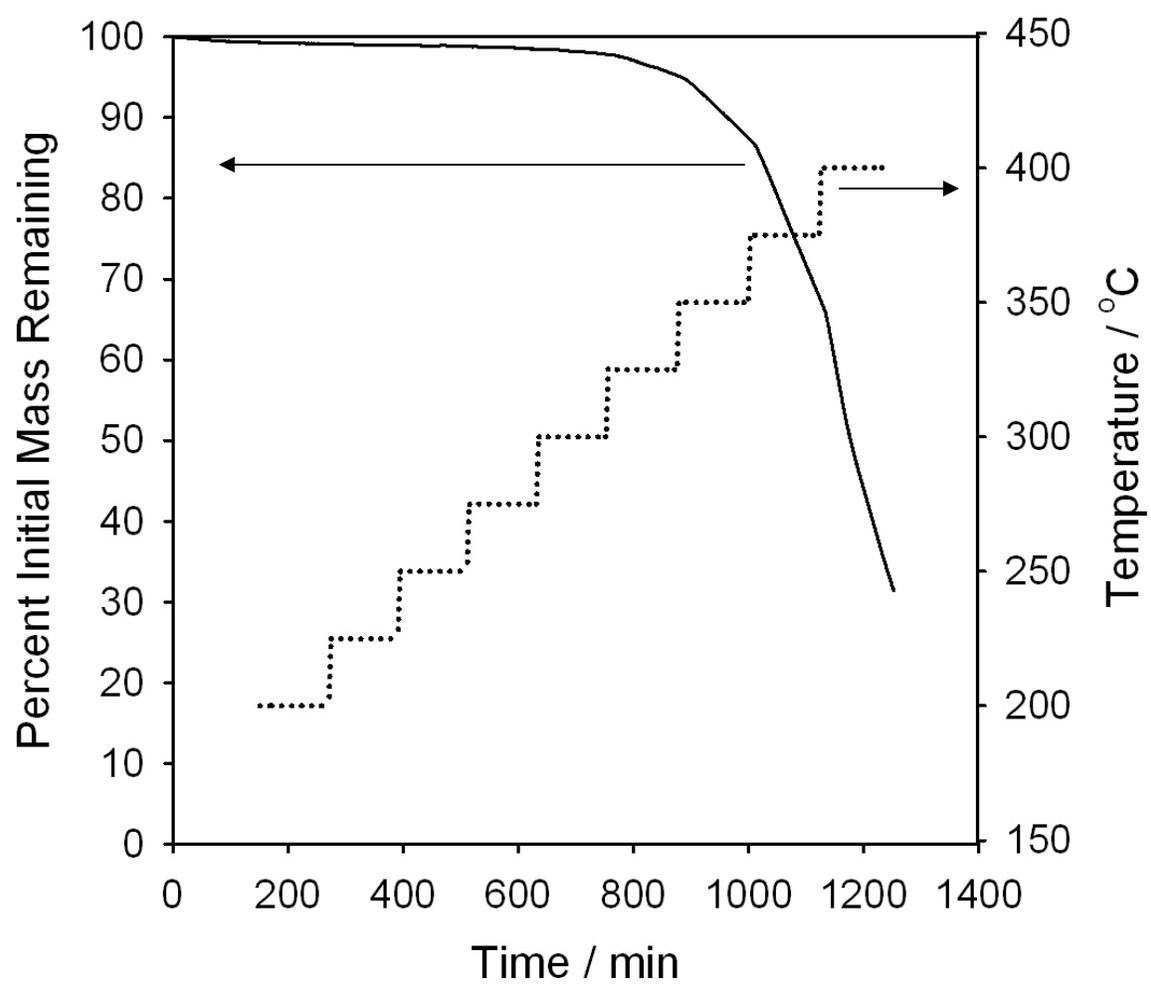
Figure 4. Example of long term heating of [C$_4$mmim][NTf$_2$] under N$_2$ atmosphere with 240 min isotherms.

	Proteus Cal. Onset (^{o}C)	5 wt. wt. lost (^{o}C)
VP-1 10 ^{o}C/min	168	125
VP-1 20 ^{o}C/min	181	133
[C$_4$mmim][NTf$_2$] 10 ^{o}C/min	459	430
[C$_4$mmim][NTf$_2$] 20 ^{o}C/min	464	443
IL w/ 0.5 wt.% Al$_2$O$_3$ 10 ^{o}C/min	447	420
IL w/ 0.5 wt.% Al$_2$O$_3$ 20 ^{o}C/min	464	445
IL w/ 1.0 wt.% Al$_2$O$_3$ 10 ^{o}C/min	438	422
IL w/ 1.0 wt.% Al$_2$O$_3$ 20 ^{o}C/min	450	434
IL w/ 2.5 wt.% Al$_2$O$_3$ 10 ^{o}C/min	428	420
IL w/ 2.5 wt.% Al$_2$O$_3$ 20 ^{o}C/min	439	431
IL w/ 0.5 wt.% CB 10 ^{o}C/min	448	424
IL w/ 0.5 wt.% CB 20 ^{o}C/min	461	446
IL w/ 1.0 wt.% CB 10 ^{o}C/min	448	410
IL w/ 1.0 wt.% CB 20 ^{o}C/min	465	439
IL w/ 2.5 wt.% CB 10 ^{o}C/min	455	424
IL w/ 2.5 wt.% CB 20 ^{o}C/min	468	449

Table 2: Thermal stability of VP-1, [C$_4$mmim][NTf$_2$], and NEILs, comparative to Proteus calculated thermal onset temperature and   5 wt.% lost.

In order to account for any deviations for previous literature values, the neat [C$_4$mmim][NTf$_2$] was evaluated thus allowing direct comparision of the enhancement (in the heat capacity) and slight decrease in thermal stability due to the addition of nano-particles into the IL. In Table 2, both a 10 C/min and 20 C/min dynamic heating rate of VP-1, [C$_4$mmim][NTf$_2$], and NEILs are compared. (All TGA experiments were conducted under a N$_2$ atmosphere using a Netzsch 209 F1 thermal gravimetric analyzer with single use Al crucibles.) The thermal analysis software (Proteus V5.2.0) calculates the thermal onset temperature based on the intersection of the baseline with the tangent, at the inflection point, of the decomposition rate. As the heat capacity of the NEIL increases (due to increased loading of the Al$_2$O$_3$), the rate of the decomposition decreases slightly due to an inherent lag in the sample heating. The lag in the heating rate of the sample will decrease the slope of the tangent, and thus the software will yeild a lower onset temperature for thermal decomposition. The 5% onset is a more accurate for the comparison of the thermal stability of different ILs, as the rate of heating in a dynamic system over-estimates the operational stability of an IL and NEIL, but is commonly reported in the literature. With the higher heating rate of 20 ^{o}C/min, there is not a significant difference in the dynamic thermal stability between the neat IL and the NEILs, as any increase in the measured thermal decomposion is probably due to the increasing lag time due to variable mass differences and/or heat capacity. At the slower heating rate, there is a slightly noticable decrease (though only a few degrees) in the onset of NEILs thermal decomposition. This could be due to better thermal conductivity of the NEILs, or possible a catalytic effect caused by the presence of nanoparticles.

References:

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