FRX Application Note Note Number : 5

Superheating Reactions

1 Summary

When using the Pressurisation Module, the FRX system can be easily pressurised up to 7bar. This allows reactions to be performed at temperatures much higher than atmospheric reflux, enabling faster and often cleaner, higher yielding reactions. This application note describes the practicalities of superheating reactions and the suggested maximum temperatures for common solvents. Typically, solvents can be heated to around 70C above their boiling point. Using the Ahrrenius rate law (doubling of rate for each 10C rise in reaction temperature), reaction rate increases of the order of 128-fold are possible.

2 Practicalities of Superheating

The boiling point of a solvent can be raised by increasing the pressure. In this way the FRX system can raise the maximum achievable temperature of a reaction by increasing the pressure by at least 7bar (from atmospheric). For example, a reaction performed in dichloromethane can be raised from a maximum of 40°C to 100°C or a reaction in acetonitrile from 82°C to 150°C.

Pressure can be generated in the FRX system by using the BPR (back pressure regulator) on the Pressurisation Module.

To apply a pressure to the output of the FRX system, the BPR needs to be connected in line immediately preceding the collection carousel. (It does not matter which way round the ports are connected.

The BPR can then be connected to the pneumatic fitting on the Pressurisation Module. The pressure applied to the BPR (0-7bar) can be varied by turning the regulator on top of the module. The BPR only allows flow when the pressure in the system has built up to the selected BPR pressure.

Backpressure can also build up due to inherent resistance to the flow. This resistance or backpressure is dependent upon a number of physical factors. Thus smaller reactor cross-section, longer reactor length, higher flow rates and more viscous liquids all generate higher backpressure. Therefore, with the BPR just “up stream” of the collection carousel the pressure in the reactor will always be equal to or greater than the BPR set pressure.

The FRX system has a maximum pressure rating of 20bar.

Typically the BPR can always be set to 7 bar. The system should be depressurised (by setting the pressure to 0) when disconnecting chips, loading sample loops, disconnecting fittings etc.

3 Estimated Maximum Temperatures for Common Solvents

Solvent	Boiling point at atmospheric pressure (°C)	Suggested max temp* @ 7bar (°C)
Acetic Acid, Glacial	118	194
Acetone	56	121
Acetonitrile	82	152
1-Butanol	118	194
2-Butanol	100	173
Chloroform	61	127
Cyclohexane	81	151
Dichlorobenzene	180	268
N,N-Dimethyl Formamide	153	236
Dimethyl Sulfoxide	189	278
1,4-Dioxane	101	174
Ether, Anhydrous	35	96
Ethyl Alcohol	78	147
Ethyl Acetate	77	146
n-Heptane	98	171
n-Hexane	69	136
Isobutyl Alcohol	108	183
Methanol	65	132
Methyl Ethyl Ketone	80	149
Methylene Chloride (DCM)	40	102
Pentane	36	97
2-Propanol	82	152
Pyridine	115	191
Tetrahydrofuran	66	133
Toluene	110	185
Water	100	173
Xylene	143	224

Note:

1) The estimated max temperature achievable at 7 bar has been calculated using the University of Cambridge website http://www.ch.cam.ac.uk/magnus/boil.html J. M. Goodman, P. D. Kirby, and L. O. Haustedt *Tetrahedron Lett.* 2000, **41**, 9879-9882.
2) There may be hazards such as degradation associated with superheating some solvents.
3) The calculated values above are an extrapolation and have not been empirically verified.
4) Solvent purity and the presence of reagents and products will change these figures, which should be seen as a guideline only.
5) *As a safety margin, a 1bar margin has been included in the above data. i.e. the suggested max values for 7 bar have actually been calculated for 6 bar.
6) Syrris provided this information for illustration only. Use the superheating capability carefully.