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Static Fluid Condensers for the Containment of Refluxing Solvent

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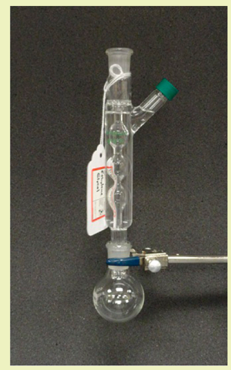
S *Supporting Information*

ABSTRACT: Allihn-type condensers have been modified to contain a fixed volume of ethylene glycol. These condensers do not require circulating fluid or bulky and expensive "heat sinks" and demonstrate acceptable solvent retention of high as well as low boiling solvents under reflux conditions. This inexpensive, effective, and "waterless" apparatus mitigates spill and flooding risks associated with circulating fluid condensers and provides a sustainable solution to the use of potable water for condensing purposes.



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INTRODUCTION

The looming shortage of potable water in the world[1,2] has prompted governments,[3] corporations,[4,5] and individuals[6] to assess their water usage, develop sustainability plans, and implement strategies to conserve this necessary but limited resource. Given that the annual freshwater withdrawal of water worldwide was 3,893.8 billion cubic meters in 2011[7] and trending to increase, efforts to conserve water are likely to become more intense.

In the practical application of synthetic organic chemistry, water is often used as a reaction solvent,[8] a purification aid to dissolve and remove byproducts, a medium to precipitate solids, or a liquid to cool reactions.[9] Indirect uses of water such as cleaning glassware, safety-related activities, employee potable uses, etc. are not discussed here. In the discovery laboratory, the use of water-jacketed condensers[10] is a very common technique to contain solvents in reactions requiring elevated heating or reflux conditions. Water is typically used because it is effective, inexpensive, and readily available. This is not to say that every condenser designed or utilized requires water as a coolant. In fact, air condensers such as Vigreux columns[11] have long been used to contain refluxing solvents in reactions. Moreover, highly engineered air condensers that contain a large metal "heat sink" have also been designed and implemented in the organic laboratory (for instance, the Aldrich Airflux condenser apparatus, catalog list price \$780.00 USD). While these approaches have a proven utility, it is a narrow one, as they are effective within a moderate temperature range. For instance, the Aldrich Airflux condenser is only recommended for solvents with a boiling point between 60 and 150 °C. In addition, the associated costs of "heat sink" apparatuses make stocking a lab impractical.

To avoid flooding risks associated with changes in water pressure from municipal sources, recirculating water systems are often employed.[12] In addition, "waterless" approaches involve the replacement of water with a nonwater circulating fluid, such as ethylene glycol. This approach is utilized by at least one major pharmaceutical company in their research laboratories. While as effective as water in containing most solvents, start-up and maintenance costs render such methods nonviable for most laboratory environments, not to mention the increased hazards associated with a spill. Herein, we wish to report a static fluid-modified Allihn-type condenser that does not require circulating liquid, water or otherwise, or bulky and expensive "heat sinks" for the containment of most common solvents employed in refluxing organic reactions.

For a reflux condenser to work efficiently the medium in the condenser needs to have a sufficient heat capacity as well as the ability to transfer the heat at such a rate as to avoid overheating. For example, running water condensers work well because water has a high heat capacity (75.327 J/mol K) and the continuous flow allows for rapid heat transfer. We recognized that the ideal choice for a non-air medium in a static fluid condenser would have a heat capacity equal or greater to that of liquid water. Additionally, this fluid would need to adequately transfer heat input out of the system, i.e., the fluid would need to have a higher boiling point than most solvents it would be asked to contain. While common alcoholic solvents have high heat capacities, e.g., ethanol has a heat capacity of 112 J/(mol K) and 1-butanol has a heat capacity of 176 J/(mol K),[13] their

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boiling points are generally less than 100 °C, effectively ruling them out. Ethylene glycol, on the other hand, has a heat capacity (149.5 J/mol K) that is higher than most substances and has an elevated boiling point of 195 °C, making this a suitable choice for our studies. The results presented in this work are not optimized with respect to static fluid medium. In fact, there are other "glycol" derivatives such as propylene glycol that could conceivably be used as well.

Another factor that was considered was the type of condenser employed in the static system. It was envisioned that a larger volume of the static liquid would be more effective at slowing any potential overheating of the condenser. Among the circulating liquid condenser body styles (West, Liebig, and Friedrich are among the many designs), the Allihn condenser has the highest volume capacity available and was therefore used for our studies. Though not necessary for function, we modified the condenser with several key functional improvements. It is worth noting that unmodified condensers may have been employed. However, Dow AgroSciences' commitment to safety provided the impetus for this redesign (Figure 1). First, to avoid the necessity of closing off a redundant inlet, only one inlet was added. Second, the remaining inlet was fabricated from a 1-dram vial fitted at a 45° angle, which served two purposes: (1) to make the operation of filling the condenser safe and simple and (2) to allow for closing the reservoir with an open top Teflon cap, thereby providing a makeshift pressure release valve in the event of overheating (Chemglass Life Sciences, ~$150.00 USD, see Supporting Information for the part number). This is accomplished by puncturing the septa with a disposable needle. The experiments performed in this study did not require this feature.

Figure 1. Modified Allihn-like condenser equipped with 24/40 adaptors.

EXPERIMENTAL SECTION

General Information. Ethylene glycol and solvents were purchased from commercial suppliers and used as received. All experiments were run using Digital Hot Plate Stirrer purchased from Chemglass Life Sciences. Aluminum blocks specifically sized for the various flask sizes were employed. All experiments were stirred at 300 rpm. Gravimetric measurements were made using either an enclosed balance (±0.0001 g) or an open balance (±0.01 g). Volumetric measurements were made using a graduated cylinder.

Typical Gravimetric Experimental Procedure. To a preweighed round-bottomed flask equipped with a Teflon-coated stir bar and a plastic cap was added the desired amount of solvent via syringe or graduated cylinder. The cap was replaced, and the flask was reweighed. The cap was removed, and the flask was equipped with the desired condenser. The system was placed under an atmosphere of nitrogen, unless otherwise noted (Supporting Information). The flask was placed into a flask-sized aluminum block that was previously equilibrated to the desired temperature. Upon visual observation of reflux, the experiment was allowed to proceed for the allotted time. Upon completion, the flask was cooled to room temperature, and the condenser was removed and the cap replaced. The flask was then weighed for a final time.

Typical Volumetric Experimental Procedure. To a round-bottomed flask equipped with a Teflon-coated stir bar was added the measured amount of solvent via a graduated cylinder. The flask was equipped with the desired condenser, and the system was placed under an atmosphere of nitrogen. The flask was placed into the flask-sized aluminum block that was previously equilibrated to the desired temperature. Upon visual observation of reflux, the experiment was allowed to proceed for the allotted time. Upon completion, the flask was cooled to room temperature, and the contents of the flask were poured into a graduated cylinder for a final visual measurement.

Use of the Condenser. Table 1 outlines a study in which we examined the feasibility of this type of condenser to contain various refluxing solvents. This is not an exhaustive study of all possible solvents but a survey of common solvents across ~150 °C boiling point range (34−180 °C). In this, 100 mL of solvent were gently refluxed in a 200 mL flask for 1 h. Less than 1% loss occurred for all solvents, including those with low boiling points. Gentle reflux is defined here as the heating device being at or about the boiling point of the solvent such that there is an observable dripping of the solvent from the condenser but not at a "rolling boil." In each experiment the choice of flask was made such that the initial solvent level was roughly

Table 1. Solvent Loss of Various Solvents, 100 mL, After 1 h at Reflux[a]

solvent	boiling point (°C)	initial solvent amount (g)	final solvent amount (g)	total solvent loss (g)	% solvent loss
diethyl ether	35	70.29	69.82	0.47	0.7
pentane	36	60.95	60.57	0.38	0.6
dichloromethane	40	130.90	130.62	0.28	0.2
THF	66	86.33	86.21	0.12	0.1
xylenes	139−144	85.65	85.60	0.05	0.1
1,2-dichlorobenzene	181	128.42	128.33	0.09	0.1

[a]The values in this table represent the average of 3 runs.

Table 2. Solvent Loss of Small Solvent Volume, 10 mL, After 1 h at Reflux[a]

solvent	boiling point (°C)	initial solvent amount (g)	final solvent amount (g)	total solvent loss (g)	% solvent loss
diethyl ether	35	6.8356	6.4731	0.3625	5.3
pentane	36	6.3590	6.0040	0.3550	5.6
dichloromethane	40	13.2200	12.9400	0.2800	2.1
THF	66	8.7960	8.6730	0.1230	1.4
xylenes	139−144	8.3830	8.3410	0.0420	0.5
1,2-dichlorobenzene	181	12.9220	12.8470	0.0750	0.6

[a]The values in this table represent one experiment per solvent studied.

Table 3. Comparative Study, 10 mL, After 18 h at Reflux[a]

solvent	boiling point (°C)	% loss [air, Vigreux]	% loss [circulating water]	% loss [static glycol]	delta % [water-glycol]
diethyl ether	35	100.0	100.0	100.0	0.0
dichloromethane	40	100.0	42.3	48.6	6.3
THF	66	100.0	37.5	40.9	3.4
acetonitrile	82	29.1	6.3	5.9	0.4
acetonitrile[b]	82	100.0	20.9	39.7	18.8
xylenes	139−144	18.3	12.0	10.3	1.7
xylenes[b]	139−144	27.6	17.0	38.6	21.6
1,2-dichlorobenzene	181	4.7	4.4	3.6	0.8

[a]The values in this table represent one experiment per solvent studied. [b]Vigorous refluxing.

half of the flask's capacity. Additionally, the condensers were proportionally sized to the size of the flask, e.g., 110 mm jacket length for a 25 mL flask with 14/20 joints.

Having demonstrated the feasibility of a static fluid condenser across a range of solvents with varied boiling points, we turned our attention to understanding the limitations of the condenser in terms of solvent amount and reflux duration. We examined small volumes, 10 mL for 1 h. Initial experiments with low boiling solvents (diethyl ether and pentane) were troubling. After 1 h, there was enough loss of solvent to predict that there would be no solvent left after a standard refluxing period of 18 h (Table 2). In fact, all solvents examined lost a higher percentage at this low volume as compared to the higher volume of 100 mL.

This increased solvent loss with lower volumes was attributed to two possibilities. The first was that a small solvent amount was an intrinsic liability with this condenser concept. The second was that a Bernoulli-like affect was siphoning the solvent out of the flask. To remove the latter from consideration, we placed the refluxing solvent under 1 atm of nitrogen to reduce the air velocity differential between the top of the condenser and the inside of the flask. To test the former, we set up a comparative experiment with an air condenser, a circulating water condenser, and an ethylene glycol filled condenser.

Table 3 outlines the results of the comparative study. Unexpectedly, none of the condensers examined were able to contain 10 mL of refluxing diethyl ether over the course of 18 h. Refluxing dichloromethane and THF also resulted in significant losses (37−48%) with both the static ethylene glycol and circulating water condenser. Only as the boiling point increased did the amount of loss drop below 20%; in most cases, the Vigreux condenser was demonstrably inferior. These data support the conclusion that small volumes of volatile solvents are an intrinsic liability with this or any condenser concept and that significant losses are likely. *Nevertheless, the results of this comparative study demonstrate that circulating water condensers and static ethylene glycol Allihn-type condensers are equally effective at containing 10 mL of solvent at reflux for 18 h, regardless of the boiling point.*

It is worthwhile to repeat that these experiments were run under gentle reflux conditions. In fact, when acetonitrile and xylenes were vigorously refluxed, a greater retention of solvent was observed with the circulating water condenser than with the static ethylene glycol condenser. When using this type of condenser setup, care must be taken to ensure that the actual heating bath temperature is near the refluxing temperature of the solvent being used to avoid overheating and greater solvent loss.

Consistent with the study of the smaller volumes, larger volumes (200−250 mL) were also contained after 18 h at reflux (Table 4). The higher boiling solvents, such as xylenes and 1,2-dichlorobenzene, as well as solvents such as dichloromethane and THF showed minimal solvent loss. Interestingly, both diethyl ether and pentane lost less than 10% of their respective volumes, representing a significant departure from their smaller volume behavior. *These data demonstrate the suitability of the condenser at larger volumes.*

Table 4. Solvent Loss of Large Solvent Volume After 18h at Reflux[a]

solvent	initial amount (mL)	final amount (mL)	total loss (mL)	% loss
diethyl ether	250	238	12	5
pentane	250	234	16	6
dichloromethane	250	244	6	2
THF	250	242	8	3
acetonitrile	250	241	9	4
xylenes	250	250	0	0
1,2-dichlorobenzene	200	200	0	0

[a]The values in this table represent the average of 3 runs.

In conclusion, the use of static ethylene glycol condensers provides a green and inexpensive method for the containment of the most common refluxing organic solvents. Even in cases where lower boiling solvents are required, these condensers show comparable solvent retention to that of circulating water condensers thus eliminating flooding concerns or the necessity to employ expensive alternative circulating fluid systems or "heat sink" systems. Finally, we would like to stress the fact that these condensers work best when a gentle reflux is employed.

ASSOCIATED CONTENT

Supporting Information

Individual measurements and pertinent calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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